

SOME MERCURY(II) COMPLEXES WITH
ORGANIC CHALCOGENE DONORS - A STRUCTURAL,
THERMODYNAMIC AND SPECTROSCOPIC STUDY

by

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A Thesis submitted in partial fulfillment
for the Degree of Doctor of Philosophy.

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Abstract Complexes of mercury(II) with thiolates in pyridine solution have been studied. Formation of three mononuclear complexes was observed in the investigated systems in dilute solution. The structures of two mercury(II) thiolate complexes in the solid state, and of three mercury(II) thiolate complexes in concentrated pyridine solution, have been determined by X-ray diffraction and scattering techniques, respectively. The first complexes show a clear tendency to polymerisation in the solid state and in concentrated pyridine solution. Complexes of mercury(II) halides, and perchlorate, with the cyclic chalcogenoethers tetrahydroselenophene (THSe) and tetrahydropyridophene (THTe) have been prepared and studied by IR and Raman spectroscopy. The crystal structures of the mercury(II) halide-THSe complexes have been determined. The chloride gives a 1:1 complex with a halogene-bridged polymeric structure. The bromide and iodide form 2:1 complexes $\text{Hg}(\text{THSe})_2\text{X}_2$ with isolated pseudotetrahedral molecules in the solid.			
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This thesis is based on the results reported in the following papers. The papers will be referred to in the text with their Roman numerals.

- I Structure of Acetato(benzenethiolato)mercury(II).
C.Stålhandske & F.Zintl; Acta Cryst. C42(1986); in print.
- II Structure of Bis(1-butanethiolato)mercury(II).
C.Stålhandske & F.Zintl; to be published.
- III Structure of (Tetrahydroselenophene)mercury(II) Chloride.
C.Stålhandske & F.Zintl; Acta Cryst. C42(1986); in print.
- IV Structures of Dibromobis(tetrahydroselenophene)mercury(II)
and Diiodobis(tetrahydroselenophene)mercury(II).
C.Stålhandske & F.Zintl; to be published.
- V Interactions of d^{10} Metal Ions and Organic Sulfur Ligands
in Nonaqueous Solvent Systems. A Thermodynamis Study on the
Complex Formation between Mercury(II) and Thiolates in
Pyridine, and between Silver(I) and Various Sulfides in
Pyridine and Dimethylsulfoxide.
F.Zintl & I.Persson; submitted to Inorganica Chimica Acta
for publication.
- VI A Structural Study of 1-Butanethiolatomercury(II) Perchlor-
ate, Pyridinium Tris(1-butanethiolato)mercurate(II) and
Pyridinium Tris(thiophenolato)mercurate(II) in Pyridine
Solution.
F.Zintl & I.Persson; submitted to Inorganica Chimica Acta
for publication.
- VII Mercury(II) Complexes with Tetrahydroselenophene and
Tetrahydrotellurophene. Vibrational Spectra.
F.Zintl; to be published.

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1. INTRODUCTION

1.1. Historical Background

In the year 1833 Zeise discovered the first thioalcohol. He saturated barium sulfide with hydrogen sulfide and heated it with calcium ethylsulfate and obtained ethanethiol as a reaction product [1]. In the same year he observed that this reacted eagerly with mercury(II) compounds like HgO and mercuric salts HgY_2 (Y=noncoordinating anion) [2]. The high affinity of the ethanethiol towards mercury(II) compounds caused Zeise to give the compound the name corpus MERcurium CAPTAns, which means the mercury snatcher. In the following time more thioalcohols were synthesized, and their chemical relationship with the alcohols became more and more known. Soon it was apparent that they form a class of organic compounds of their own, and that they have the high affinity towards mercury(II) compounds in common.

Since it was clear that they all were "mercury snatchers", and that this property was caused by the presence of the -SH functional group, they were awarded the common name "mercaptans", which was a contraction of Zeise's nickname for the ethanethiol. The thioalcohol group -SH was soon called mercapto group, and the metal salts derived from these thiols were called mercaptides.

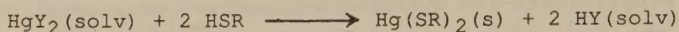
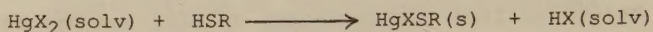
Zeise realized that he had discovered more than merely a new kind of functional group, and a new class of organic compounds. He had discovered a love story: the love story between mercury and thiol.

Soon it was also obvious that there were more analogues like that: the thioethers which correspond to ethers in the same way as the thiols do to alcohols, were also discovered by Zeise [2a,3] and Döbereiner [4] at the same time. Also these compounds have high affinity towards mercury(II) compounds, as soon thereafter was observed.

In the following decades the picture became more and more complete. The differences between the two compounds series became apparent, too.

While the thiols are weak acids, and lose their proton bonded to the sulfur atom when they react with the mercury(II) compounds, the thioethers have no such possibility.

Thus the reaction between thiols and mercury(II) compounds is a salt formation



which reaches different steps for halides X and for salts of less coordinating anions Y, like carboxylates, nitrate, perchlorate, tetrafluoroborate, sulfonates etc. [5a].

The two equations above describe the formation of end products which are insoluble in, and precipitate from the solvent.

This is the case when these reactions are carried out in aqueous media or in organic oxygen donor solvents like alcohols, ketones, and ethers. In solvents where the mercury(II) thiolate complexes are well soluble, like in liquid ammonia or in some organic nitrogen donor solvents, the reaction pattern can be quite different, and consequently lead to different end products as well (see 3.1.1. and [V]).

On the other hand, the reaction with thioethers [5b] is a pure complex formation between the metal acceptor and the neutral ligand, following the pattern



In the latter reaction the ratio x/y in the final product is partially controlled by the donicity of the anion X, but other influences, like the size and donicity of the thioether, and the choice of the reactive medium, seem to be of the same importance.

Today it is well known that thiols and thioethers are also very fond of some other heavy metal ions, like e.g. copper(I), silver(I), gold(I), and lead(II). All these metal acceptors, except lead(II), have two things in common:

1. a $d^{10} s^0$ closed outer shell with pseudo noble gas electron configuration and
2. a relatively high polarizability of this outer electron sphere.

The metal ions with these properties were systematized by Ahrland, Chatt and Davies [6] , and by Pearson [7] , as the class (b) (soft type) metal acceptors.

Something similar was stated concerning common properties of the thiols and thioethers. Thioketones and other organic compounds with C=S groups also show affinity to mercury(II) as thioethers, and so do the selenoethers and telluroethers [8-10] .

Even selenoalcohols and telluroalcohols, which contain the functional groups -SeH and -TeH, respectively, are known to behave in a similar way as the thiols towards mercury(II), and some complexes were synthesized and described in literature (see below). All that indicates that these compounds, when brought into contact with the metal ions mentioned above, have common properties which cause them to behave similarly in comparable chemical situations.

The same concept which was applied to the metal acceptors is applicable for these compounds, as far as their donicity towards those metal acceptors is concerned. All these organic compounds were, analogously to the metal ions, systematized as so called class (b), or soft type, donor systems. Expressing the observations in a simple manner one can say that soft type donors are especially fond of soft type metal acceptors, and readily coordinate to them via interactions with a high degree of covalency, and often in polyhedra which produce coordination numbers 2-5 [6,7] .

During one hundred years after the first observations the complex compounds of chalcogenoethers $RChR'$ and of chalcogenoalcohols $RChH$ ($Ch = S, Se, Te$) with mercury(II) were prepared mainly to characterize the organic substances via their derivatives, e.g. by means of their melting points [5] . The mercury complexes themselves were paid attention rather late, and more as a consequence, than as a foregoing work, of the general concepts mentioned above.

1.2. Mercury(II) as a Metal Acceptor

Most of the studies investigating complexes of mercury(II) with soft type ligands are well compiled in rather recent reviews [8-21]. Some of these reviews contain a systematic overview about certain types of metal complexes, like with chalcogenoligands in

general [8] or with chalcogenoethers in special [9], with thiols and thioketones [10], mercaptoamino acids [11], complexes with organic telluro ligands [12] and with proteins [14]. Others preferably contain results from special investigation methods, like results from crystal structure determinations [17,18], and in some cases include even other metals than mercury [8-14].

A good review of the mercury chemistry until 1975-6 is given by McAuliffe [22], and the annual reviews by Hughes [20] and Constable [21] provide results reported in literature after that time. It is noteworthy that the book about organotellurium chemistry written by Irgolic [23] also contains a lot of information about mercury(II) compounds. The properties of the chalcogenoorganic ligands as chemical compounds are described in [5] and [23-25].

It is useful to mention all these sources since they supply the reader with many facts which, thanks to these reviews, need not separately be discussed here.

While the structural, spectroscopic, and thermochemical properties of mercury(II) halide complexes with neutral pnictogen (N,P,As,Sb) or chalcogen (O,S,Se,Te) ligands have been very well compiled in some of the above mentioned reviews [8,9,15,16], a systematic collection of e.g. spectroscopic and structural material on mercury(II) thiolate, selenolate, and tellurolate complexes is still missing.

Since mercury(II) thiolate complexes are one of the central topics of this work, it seems reasonable to give a small survey of the most important structural data concerning solid complexes of mercury(II) which contain at least one Hg-SR bond (Table I). Structural data on analogous selenolate or tellurolate complexes, and results from own works [I,II], have been included in suitable positions. Derivates of organomercurials RHg(II)^+ , and mixed halogenothiولاتomercury(II) complexes of the general type Hg(SR)X , so called "half mercaptides" [5a], were not taken into account since they are not of central importance in the context of this investigation.

It is clearly seen that mercury(II) in the compounds in Table I prefers the coordination numbers 2-5 for pure sulfur coordination, and 5-6 in cases of mixed coordination.

The formal 1:1 mercury-thiolate complexes $[\text{HgSR}]\text{O}_2\text{CCH}_3(\cdot\text{L})$, which in some cases crystallize with one solvent molecule L per formula unit, achieve linear or bent two coordination by sulfur by forming chains of the type $(-\text{Hg}-\text{SR}-\text{Hg}-\text{SR}-)$ [26-28;I]. In the complexes without solvent molecules L the effective coordination of the mercury is increased to five or six by coordinating oxygen atoms from the acetate ions [26,27,I]. In the complexes containing one pyridine or 4-methylpyridine solvent molecule per formula unit all mercury atoms are five coordinated, by two thiolates, two oxygens from one acetate, and one solvent nitrogen [26,28] .

In the 2:1 complexes two [31,32,35], four [34,36,II] , five [29,30] and six [31,34] coordination have been found around the mercury ions. In the cases of coordination numbers 5 or 6 , however, usually two or more of these contacts are so long that it seems questionable to assign any bond character to them.

Examples for 3:1 complexes with three coordination [40] and with four coordination [38,39] of the mercury(II) ion have been reported.

One 4:1 complex with four coordination has been found in the pseudotetrahedral tetrakis(4-chlorobenzenethiolato)mercurate(II) [42].

These results agree with those found for the complex formation between mercury(II) and other soft type ligands, like uncharged chalcogeno ligands, bromide, iodide, and pseudohalogenide ions, phosphines, arsines, and stibines and in some systems even chloride ions. The same tendency towards "medium" coordination numbers is also seen for selenolate [37] , or tellurolate [41] , complexes of mercury(II). In this field, however, the number of observations literature is still poor, probably due to the high sensitivity of these ligand systems towards oxygen and moisture [24] .

TABLE I: Some Structural Data on Mercury(II) Thiolate and Mercaptide Complexes

Compound or Complex	Coord. number	Structure principle	Distances around the Mercury(II) (pm) (only bonds and close contacts to Hg)	Ref.
$[\text{HgSCH}_3]_2\text{O}_2\text{CCH}_3$	5 and 6	Infinite chains of	S: 238.7, 240.5; O: 242, 282, 270	[26]
$[\text{HgS}^{\text{I}}\text{C}_3\text{H}_7]_2\text{O}_2\text{CCH}_3$	5 and 6	$[-\text{Hg}-\text{SR}-]$ units	S: 241, 240; O: 242, 2*276, 314	[27]
$[\text{HgS}^{\text{II}}\text{C}_4\text{H}_9]_2\text{O}_2\text{CCH}_3$	5 and 6	connected to sheets	S: 240, 242; O: 247, 278, 286, 298	[27]
$[\text{HgSC}_6\text{H}_5]_2\text{O}_2\text{CCH}_3$	5 and 6	by acetate ions.	S: 240.3, 241.0, 244.5, 248.1; O: 248.3, 255.1, 251.4, 285.2, 287.3, 237.8, 256.9	[1]
$[\text{HgSCH}_3]_2\text{O}_2\text{CCH}_3 \cdot \text{Py}^1$	5	Infinite isolated	S: 247.1, 242.2; O: 243, 269; N: 246	[26, 28]
$[\text{HgSCH}_3]_2\text{O}_2\text{CCH}_3 \cdot 4\text{-MePy}^2$	5	$[-\text{Hg}-\text{SR}-]$ chains with one nitrogen	chain a: S: 247.1, 241.4; O: 244, 266; N: 249	[28]
$[\text{HgSC}_2\text{H}_5]_2\text{O}_2\text{CCH}_3 \cdot \text{Py}^1$	5	ligand coordinated to each Hg-atom.	chain b: S: 245.9, 247.3; O: 237, 280; N: 241 S: 241.4, 245.2; O: 241, 261; N: 266	[28]
$\text{Hg}(\text{SCH}_3)_2$	5	Linear RS-Hg-SR	S: 2*236, 4*325	[29, 30]
$\text{Hg}(\text{SC}_2\text{H}_5)_2$	2 or 6	molecules with ad-	S: 2*245, (4*354)	[31, 32]
$\text{Hg}(\text{SC}_2\text{H}_4\text{CONHCH}_3)_2^3$	4 or 6	ditional contacts	S: 2*235, 2*325, (2*360)	[33]
$\text{Hg}(\text{SC}_6\text{H}_4\text{CO}_2\text{H})_2 \cdot \text{dioxan}^4$	6	to S- or O- atoms.	S: 2*236.1; O: 2*311, 2*308	[34]
$[\text{Hg}(\text{SCHC}_4\text{H}_8\text{NCH}_3)_2](\text{ClO}_4)_2^5$	2	Linear ions.	S: 2*232.9	[35]

TABLE I: (continued)

$\text{Hg}(\text{S}^{\text{C}}\text{H}_9)_2$	4	Distorted HgS_4 or	S: 2*259, 2*266	[36]
$\text{Hg}(\text{SeCH}_3)_2$	4	HgSe_4 tetrahedra	Se: 262.5, 261.4, 276.4, 265.9	[37]
$\text{Hg}(\text{S}^{\text{N}}\text{C}_4\text{H}_9)_2$	4	linked via sulfur (selenium) ligand	S: 248.2, 252.2, 254.9, 262.8 S: 250.0, 252.4, 253.5, 258.4	[II]
$(\text{NET}_4)_2[\text{Hg}_2(\text{SCH}_3)_6]$	4	bridges.	S: 243.8, 247.3, 262.9, 270.6	[38]
$(\text{PPh}_4)_2[\text{Hg}_3(\text{SC}_2\text{H}_4\text{S})_4]$	4	Distorted HgS_4 -tet-	S: 2*236.3, 2*237.1, 2*254.5, 2*256.3, 2*285.2, 2*286.4	[39]
$(\text{PPh}_4)_2[\text{Hg}_2(\text{SC}_2\text{H}_4\text{S})_3]$	4	rahedra (see [39]).	S: 2*242.0, 2*244.2, 2*267.4, 2*272.2	[39]
$(\text{NET}_4)[\text{Hg}(\text{SC}_6\text{H}_5)_3]$	3	Isolated trigonal	S: 240.7, 243.1, 250.7	[40]
$(\text{PPh}_4)[\text{Hg}(\text{TeC}_6\text{H}_5)_3]$	3	planar HgL_3^- -ions.	Te: 268.2, 269.2, 271.7	[41]
$[\text{Hg}(\text{SC}_6\text{H}_5)_3]^-$ in Py	3 or 5	Trigonal planar	S: 3*247.5; C: 3*376	[VI]
$[\text{Hg}(\text{S}^{\text{N}}\text{C}_4\text{H}_9)_3]^-$ in Py	3 or 5	$\text{Hg}(\text{SR})_3$ -anions.	S: 3*245.5; C: 3*369	[VI]
$[\text{Hg}(\text{S}^{\text{N}}\text{C}_4\text{H}_9)_2\text{Hg}]^{2+}$	2, 4 or 6	Tetragonal planar $\text{Hg}_2(\text{SR})_2$ -dimers.	S: 2*249, Hg: 1*369; C: 2*375	[VI]
$(\text{Me}_4\text{N})_2[\text{Hg}(\text{SC}_6\text{H}_4\text{Cl})_4]$	4	Distorted isolated tetrahedra.	S: 2*253.7, 2*255.2	[42]

1. Py: pyridine.

2. 4-MePy: 4-Methylpyridine (γ -picoline)

3. Bis(methylcarbamoylthiolato)mercury (II)

4. Bis(2-mercaptobenzoato-S)mercury (II) Monodioxane

5. Bis (N-methylpiperidinium-4-thiolato)mercury (II) perchlorate

6. data from concentrated pyridine solutions.

For structural, spectroscopic, and other data on mercury(II) chalcogenoether complexes see McAuliffe [22], Irgolic [23] and some reviews [9,16]. Data on complex formation between organic ligands and mercury(II) in solution have been compiled in the books by Sillén & Martell [43a], by Perrin [43b], and by Martell & Smith [44]. Some data on the complex formation between mercury(II) and substituted thioethers and polythioethers in aqueous media have been contributed by Widmer [45]. It is obvious from these sources that the mercury in solution never is more than four coordinated by sulfur ligands. Generally the mercury(II) ion can choose between all coordination numbers between 2 and 6, which can be explained with its closed outer electron shell.

A more precise explanation, especially for its tendency to form stable compounds with linear two coordination, and sometimes three or four additional contacts on larger distances, has been given by Orgel [46] and Nyholm [47]. Their explanation is based on the small $5d^{10} \rightarrow 5d^9 6s^1$ separation. This means nothing else than that the difference in energy between these two electron states is small. As a consequence, the $5d_z^2$ and $6s$ orbitals can mix to two degenerate new sd_z hybrids almost without loss of energy. If one of these sd hybrids is filled with two electrons, the other one with its orientation along the z -axis will be empty, and thus produce high electronegativity along this direction. This means that nucleophiles are attracted along this axis, and will therefore preferably approach the metal acceptor from opposite sides, and produce linear coordination. The result is opposite to the first order Jahn-Teller effect of d^9 or d^4 systems: axial coordination on short distances is paired with equatorial coordination on long distances [26-34, I]. In cases of mixed coordination it is observed that the mercury(II) ion chooses to add the softer donor atoms axially on the short distances, and to contact the harder donor atoms only loosely in the equatorial plane, on long distances [26-28, 34, I].

1.3. The Scope of this Work

Since copious structural and spectroscopic data are available on solid complexes between mercury(II) compounds and soft type sulfur ligands, it seems useful to complete them by observing the complex formation reactions in suitable solvent systems. The structural data only give the shape of the complexes, which often is different from what it is in solution where no distortions by packing effects can occur. Moreover, parametra like stabilities of bonds can be derived from crystal structures only very qualitatively, following the assumption that a closer contact, i.e. a shorter bond, indicates greater stability.

The determination of the complex formation constants β_j , however, gives the free complex formation enthalpies ΔG°_j which contain the thermodynamic stability of the complex HgL_j , and therefore allow an approach to the relative stability of the bonds in a given solvent system. When the complex formation enthalpies ΔH°_j are determined additionally, the complex formation behaviour of mercury(II) with the corresponding ligand L in the given solvent can be completely described in terms of enthalpy and entropy changes. The enthalpy changes are correlated with the energy which is consumed, or set free, during the bond formation. The entropy changes are correlated with the changes of order around the metal ions. The solvent affects the complex formation reactions which are specific for the solvent system and might be different in an other solvent.

Still the complex formation enthalpies and entropies can be compared internally, if several complexes are formed, even if data for the same metal-ligand system in other solvents are not available, and thus no external comparisons are possible.

It seemed therefore reasonable to determine the complex formation constants, enthalpies, and entropies for reactions between mercury(II) and some sulfur ligands.

Two thiols, 1-butanethiol and thiophenol, and their sodium salts, were chosen for that purpose.

Since the mercury(II) complexes which are formed with this type of ligands have low solubility in water, and even in a number of

organic solvents, a suitable solvent had to be found in which both initial compounds and the reaction products are sufficiently soluble. Pyridine was found to fulfill this condition.

For determination of the formation constants β_j potentiometric measurements were performed, for the determination of the complex formation enthalpies ΔH°_j calorimetric titration was applied. The thermodynamic equations $-\Delta G = RT \ln K$ and $\Delta S = (\Delta H - \Delta G) T^{-1}$ allow the calculation of the quantities ΔG°_j and ΔS°_j . All measurements were performed at the same temperature $T = 298K$, i. e. at standard conditions (see 3.1.1., 3.1.3 and [V]).

After determination of the number, and relative stabilities, of the complexes which are formed between mercury(II) and 1-butanethiolate, or thiophenolate, ions in pyridine, three of these complexes were chosen for structure determination in solution by means of X-ray scattering measurements. The Large Angle X-ray Scattering (LAXS) method was applied, and the structures for the two anionic complexes $[Hg(SR)_3]^-$ ($R = {}^n C_4H_9, C_6H_5$) and of one cationic complex " $HgS^{}^n C_4H_9^+$ " in concentrated pyridine solution were determined (see 3.1.2. and [V]).

The crystal structures of two solid mercury(II) thiolate complexes, acetatobenzenethiolatomercury(II) and Bis(1-butanethiolato)-mercury(II), were determined [I, II].

These structures had not yet been reported in literature except for a preliminary investigation on $Hg(S^{}^n C_4H_9)_2$ [32]. They also constitute a good complement to previous works (see Table I).

So far the first aim of this investigation was to describe the complex formation between mercury and sulfur ligands, mainly thiolate anions, by means of thermodynamic and X-ray measurements.

The second aim was to compare the donor properties of organic sulfur, selenium, and tellurium compounds by determining their relative affinity towards mercury(II) ions.

Unfortunately the selenols and tellurols are extremely sensitive to air oxygen and moisture [24]. They can therefore not be used as ligand systems in thermodynamic measurements. The selenoethers and telluroethers are, on the other hand, more stable in air.

Since efforts to determine the complex formation constants of mercury(II) with some thioethers in pyridine and dimethylsulfoxide(DMSO) failed, it seemed not very promising to apply the same methods to seleno- and telluroethers.

Consequently the approach was changed. The cyclic chalcogenoethers tetrahydrothiophene(THT), tetrahydroselenophene(THSe) and tetrahydrotellurophene(THTe) were chosen as analogous compounds.

The complexes of mercury(II) halides with THT are well known, a number of structures in the solid state and in THT solution have been solved [48-50], and vibrational spectra have been reported [50-52]. Based on these previous investigation the same pathway was followed for the THSe and THTe complexes of the mercury(II) halides. Additionally, the solvates $[\text{HgL}_x](\text{ClO}_4)_2$ were prepared for $\text{L} = \text{THT}; \text{THSe}$ and THTe (see 3.2.1. and [VII]).

Ir and Raman spectra were recorded on all defined complexes, and on the solutions of the mercury(II) halides in THSe, as far as possible (VII). Here it was helpful that a complete treatment of the vibrational spectra of the three ligands was given in the literature [53].

Single crystals were obtained of three complexes, $\text{Hg}(\text{THSe})\text{Cl}_2$ and $\text{Hg}(\text{THSe})_2\text{X}_2$ ($\text{X}=\text{Br}, \text{I}$) and their crystal structures solved [III, IV].

2. EXPERIMENTAL SECTION

2.1 Chemicals

For preparation and composition of chemicals and solution see [I-VII]:

- [I] : preparation of $[\text{HgSC}_6\text{H}_5]\text{O}_2\text{CCH}_3$ (single crystals).
- [II] : preparation of $\text{Hg}(\text{S}^n\text{C}_4\text{H}_9)_2$ (single crystals).
- [III] : preparation of $\text{Hg}(\text{THSe})\text{Cl}_2$ (single crystals).
- [IV] : preparation of $\text{Hg}(\text{THSe})_2\text{X}_2$ ($\text{X}=\text{Br}, \text{I}$; single crystals).
- [V] : purification of solvent and ligands, and preparation of compounds and solutions for electrochemical and thermochemical measurements on the systems $\text{Hg}(\text{ClO}_4)_2\text{-HSR}(\text{NaSR})$ and $\text{AgClO}_4\text{-SR}_2$ in pyridine, and on $\text{AgClO}_4\text{-SR}_2$ in DMSO.
- [VI] : preparation of solutions for X-ray scattering measurements on the system $[\text{Hg}(\text{SR})_3]^-$ ($\text{R}=\text{C}_4\text{H}_9, \text{C}_6\text{H}_5$) and $[\text{HgS}^n\text{C}_4\text{H}_9]^+$ in pyridine.
- [VII] : preparation of the ligands tetrahydroselenophene (THSe) and tetrahydrotellurophene their complexes with mercury(II) halides and perchlorate, for (THTe), and of spectroscopic investigation.

2.2 Determination of Thermodynamic Functions

2.2.1 Potentiometric measurements

The stability constants β_j for the stepwise complex formation of mercury(II) perchlorate with thiophenol, 1-butanethiol, their sodiumsalts, and the thioethers Ph_2S , $^n\text{Bu}_2\text{S}$, and THT, in dilute pyridine solutions ($\text{C}_{\text{Hg}} < 16\text{mM}$) were determined using potentiometric titrations.

All determinations were performed as central ion measurements.

A silver plate electrode in a 10 mM AgClO_4 solution in pyridine was used as reference cell.

A liquid mercury pool served as a working electrode. The titrations had to be performed in reverse order: a mercury(II) perchlorate solution containing excess of the ligand was titrated with a mercury(II) perchlorate solution without ligand. The reasons for this method are given in [V].

Since complex formation between mercury(II) and the thioether ligands was not observed, their ability as donor systems was checked by determination of the complex formation constants between them and AgClO_4 in both pyridine and DMSO solution.

Here the potentiometric titrations were performed in the usual way: a solution of the ligand was added in small portions to a solution of the metal salt. Even here the details are given in [V]. Efforts to determine the stepwise complex formation constants of silver(I) with the thiols and sodium thiolates were unsuccessful due to the low solubilities of the neutral compounds AgSR ($\text{R}=\text{Ph}$, ^nBu) in pyridine.

All potentiometric titrations were performed in glove boxes in thermostated reaction vessels at 25°C.

2.2.2. Calorimetric Measurements

The enthalpy changes during the stepwise complex formation between mercury(II) and the thiols and sodium thiolates in pyridine, and between silver(I) and THT in DMSO, were determined by calorimetric titration. Direct titration were performed on all these systems. The routine and the calorimeter have been described elsewhere [5]. For details see [V].

2.2.3. Calculations

For all calculations of the thermodynamic quantities from the raw data ready computer programs were available. The complex formation constants β_j were calculated from the emf's from the potentiometric titrations.

The programs EMK [55] and EMKBAK [55] were used for this purpose. For the way of their application, and the difference between them, see [V] and the references therein. From the complex formation constants β_j , the stepwise formation constants K_j and the free enthalpies ΔG°_j were obtained from the equations $\beta_j = \prod K_j$ and $\Delta G^\circ_j = -RT \ln K_j$ (with $T=298.15$ K). The enthalpy changes ΔH°_j were calculated from the heats obtained from the calorimetric titrations. The computer program KALORI [56] was used; the β_j values were taken from the results from potentiometry and introduced as fixed parametra. From the results the stepwise complex formation entropies ΔS°_j were calculated by hand according to the equation

$$\Delta S^\circ_j = (\Delta H^\circ_j - \Delta G^\circ_j) \cdot T^{-1}.$$

The limits of error were given with three standard deviations [30] for the β_j and ΔH°_j values [V].

2.3. Methods based on X-ray Techniques

2.3.1. X-Ray Diffraction Measurements

For all X-ray diffraction measurements MoK_α -radiation with wavelength $\lambda=71.07\text{pm}$ was used.

Crystal structures were determined for the compounds

$[\text{HgSPh}]_2\text{O}_2\text{CCH}_3$	[I]
$\text{Hg}(\text{S}^n\text{C}_4\text{H}_9)_2$	[II]
$\text{Hg}(\text{THSe})\text{Cl}_2$	[III]
$\text{Hg}(\text{THSe})_2\text{X}_2$ (X=Br, I)	[IV].

The compounds in [II] and [IV] had to be sealed in narrow tubes of Lindemann glass together with a little mother liquid.

The data were collected on an Enraf-Nonius-CAD4 diffractometer equipped with a graphite monochromator; ω -2 θ -scans were performed for all compounds. The determination of the cell constants were based on 25-50 2 θ -values measured on the same instrument.

Direct methods were applied on all structures using available computer programs [57,58a,b]. For the compounds in [IV] Patterson syntheses were used additionally to check the results from the direct methods [58a].

Lp and absorption corrections were performed, and the latter were based on the crystal geometries. Full matrix least square refinements were applied to minimize $\sum w(F_o - F_c)^2$ with weights

$$w = [\sigma^2(F_o) + (C_1 F_o)^2 + C_2]^{-1} \quad (C_1 = 0.03 - 0.06; C_2 = 0 - 2.5).$$

Selected H-atoms were included in calculated positions $d(C-H) = 100 \text{ pm}$ in some of the final refinements [I, II, III].

Anisotropic thermal parameters β_{ij} were refined for all atoms except carbon and hydrogen and, where possible, even for carbon atoms.

For details see [I-IV], and references therein.

2.3.2. Large Angle X-ray Scattering Measurements on Solutions

The structures of the two anionic complexes $[\text{Hg}(\text{SR})_3]^-$ ($R = \text{Ph}, ^n\text{Bu}$) in high concentrations were examined using X-ray scattering from the free surface of the solutions.

With the same method the structure of the first complex " $[\text{HgS}^n\text{C}_4\text{H}_9]^+$ " in pyridine solution was determined to a dimer $[\text{Hg}(\text{SR})_2\text{Hg}]^{2+}$.

All samples were kept at a constant temperature of 25°C during the measurement.

The data were collected on a Seifert GDS θ - θ -diffractometer.

MoK α -radiation of wavelength $\lambda=71.07\text{pm}$ was used.

The intensities were measured in a time dependent scale: the time for the collection of $4 \cdot 10^4$ counts was registered twice for each θ -value. For details see [VI] and references therein.

2.4. Vibrational Spectra

Infrared spectra were recorded on a Perkin-Elmer 580B Infrared Spectrophotometer equipped by the manufacturer with a Data Station 3600. Solid samples were prepared as polyethylene tablets or as Nujol mulls between CsBr-plates. Solutions were recorded between parallel polyethylene windows; a constant distance of 0.5 mm was kept with a spacer. The wavenumber region between 4000 and 200 cm^{-1} was accessible; numeric corrections for the Nujol background were performed when necessary.

FIR spectra were recorded on a Bruker 113V FTIR spectrometer. The wavenumber region from 700 to 100 cm^{-1} was covered by this method. Only solid samples were recorded; they were prepared as polyethylene tablets.

All Raman spectra were excited with radiation from a Kr^+ -ion laser; the red line at $\lambda=647.1\text{ nm}$ was used.

A part of the spectra were recorded on Cary 82 and Spex Raman spectrometers; both were equipped with a Spectra Physics 164 Kr^+ -laser. The remaining spectra were registered on a D.I.L.O.R. RTI-30 Raman spectrophotometer equipped with a triple monochromator, a dc-amplifier and a Coherent Radiation Laboratories Innova 90-5 Kr^+ -laser.

The spectral bandwidth was varied between 2 and 10 cm^{-1} according to the requirements during the measurements. Solid samples were sealed in narrow glass tubes, solutions were filled into usual small glass tubes with an inner diameter about 5 mm or in cubic glass cells with the same dimensions.

3. RESULTS

3.1 Mercury(II) and Charged Sulfur Ligands

3.1.1. Complex Formation in Solution

Mercury(II) perchlorate forms three mononuclear complexes $[\text{Hg}(\text{SR})_x]^{2-x}$ ($x=1-3$) with the thiols PhSH and $^n\text{BuSH}$ and with their sodium salts in dilute pyridine solution.

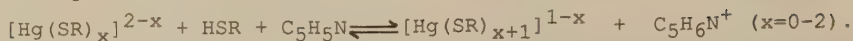
The β_j values ($j=1-3$) from the potentiometric measurements are listed in Table II in [V], the ΔH°_j values ($j=1-3$) from the calorimetric titrations are given in Table III in [V]. The limits of error in both Tables refer to three standard deviations.

In Table IV in paper [V] the thermodynamic functions which are accessible from the data in the preceding Tables are listed. Hence it is clearly seen that all $\log K_j$ values are of the same order of magnitude for all complexes in all four systems. The complex formation curves of the systems with the sodium thiolate ligands are shown in Fig.3 in [V] and the complex distribution curves in the same systems are given in Fig.4 in paper [V] as functions of the decadic logarithm of the free ligand concentration, $\log [L]$.

The corresponding curves for the systems with the free thiols as ligands are so similar to those for the sodium thiolates that they were not shown separately.

It seems surprising on the first view that the complex formation constants are so similar for the sodium thiolates and for the free thiols. Probably the same complexes with mercury(II) are formed independently whether the ligand sulfur atom initially bears a hydrogen atom or not. If this is the case, an explanation must be found for what is happening to the thiol hydrogen during, or prior to, complex formation. Since the solvent pyridine is known as a nitrogen base which can receive H^+ ions from proton acids and form pyridinium salts according to $\text{C}_5\text{H}_5\text{N} + \text{HX} \longrightarrow \text{C}_5\text{H}_6\text{N}^+ + \text{X}^-$, it is suggested that the pyridine acts as a supporting base during

the complex formation following a similar equation



This reaction is the more likely the more acidic the S-bonded hydrogen atom is in the given thiol. Anyhow, this reaction seems to take place and play its role comparably well both for the thiophenol and for the 1-butanethiol ligand.

The complex formation between mercury(II) perchlorate and organic thiols or sodium thiolates shows some surprising properties:

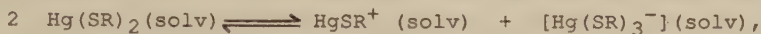
1. No formation of a fourth complex $[\text{Hg}(\text{SR})_4]^{2-}$ has been observed.

This is remarkable since mercury(II) usually forms four mononuclear complexes $[\text{HgX}_x]^{2-x}$ ($x=1-4$) with the halogenide ions in water, aqueous alcohols, DMSO, and pyridine. In all these solvents, except the pyridine itself, formation of four mercury(II) complexes was also observed with the thiocyanate anion which in all solvents coordinates the mercury as a sulfur ligand. In pyridine, however, only three thiocyanate complexes with mercury(II) are formed [60].

Since all these observations are a picture of the competition between donor strengths of the solvent molecules and the ligand anions, it seems reasonable to assume that the solvent pyridine is strong enough to suppress the formation of a fourth complex between thiolate and thiocyanate anions, and mercury(II) cations, while the formation of such a complex is not suppressed by the weaker donors DMSO and alcohols, or for the smaller halide anions which possess a higher charge density and are less bulky.

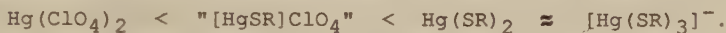
2. The K_1/K_2 and K_3/K_2 (see Table III in [V]) indicate that the systems are predominated by the first or the third complex for very small and large $[\text{L}]$ values, respectively. The formation of the second complex is widely suppressed, and in no case exceeds 45% predominance. This can clearly be seen from the complex distribution curves, too (see paper [V]). This behaviour is a picture for what is happening when the neutral compounds $\text{Hg}(\text{SR})_2$

are dissolved in pyridine, and probably even when they are dissolved in other liquid N-donors. They will dissociate according to the equation



the equilibrium constant K for this reaction being in the region between 0.4 and 1. This may be the reason why the mercury(II) thiolates are well soluble in pyridine and in many amines while they are less soluble in O-donating solvents like alcohols, ketones, and ethers, and practically insoluble in water.

3. The different steps of complexation show different solubilities in pyridine following the sequence:



The concentrations of the solutions used for potentiometric and calorimetric titrations were thus limited by the solubility of the mercury(II) perchlorate in pyridine ($L=16\text{mM}$), and the results obtained from these measurements are a picture only of the processes in these diluted solutions.

It is uncertain how these results are applicable even to saturated or close-to saturated solutions with the same ligand:mercury ratio. Formation of dimeric complexes was observed in one case where no dimerisation had stated in the dilute system (3.1.2 and [VI]).

The sequence of solubilities in (3.) is interesting since the opposite order is observed for silver(I) in the same solvent. The neutral silver(I) thiolates are practically insoluble in pyridine, while about 0.5 mol silver(I) perchlorate can be dissolved in pyridine at room temperature [61].

3.1.2. Structural Data from Pyridine Solutions

The structures of the anionic complexes $[\text{Hg}(\text{SR})_3]^-$ ($R=\text{Ph}, ^n\text{Bu}$) and of the cationic complex $"(\text{HgS}^n\text{Bu})^+"$ in concentrated pyridine solutions were determined with X-ray scattering investigations

according to the LAXS-technique [59]. For details of the method, measurements, and calculations, see [VI] and references therein. The mercury(II) sulfur, sulfur-sulfur, mercury-carbon, and mercury-mercury distances are listed in Table II in [VI]. In the anionic complexes the sulfur atoms surround the mercury ion in the corners of an equilateral triangle, the mercury occupies the center of gravity. The raw data allow no refinements for other than short Hg-S, S-S, and Hg-C distances. Theory for equilateral triangles gives a ratio

$$d(\text{Hg-S})/d(\text{S-S}) = 0.5774.$$

This requirement is well fulfilled in both anionic complexes. It is likely that the triangular complexes are completed to regular trigonal bipyramids by axial pyridine coordination. The data material is, however, not of sufficient quality to allow a certain decision whether, and on what distance, the pyridine molecules coordinate axially to the central mercury ions.

The data material does not allow any refinements of the distances of the thiolate hydrocarbon skeletons either. The sulfur-carbon distances were set to 183 pm, which was an average value from a number of structural data on thiolate anions contained in other compounds [26-28,33-35,38,40,42,62-65,I,II].

The carbon-carbon distances were set to 154 pm for the n-butyl groups and to 138 pm in the aromatic ring system of the thiophenolate anion.

Axial pyridine coordination, if it occurs on the trigonal planar anionic $[\text{Hg}(\text{SR})_3]^-$ complexes, might be the explanation why no formation of a fourth complex was observed in this solvent: it seems that the thiol(ate) ligand is not competitive to substitute the axial solvent molecules (see 3.1.1) under formation of a higher complex. Except the rather good donicity of the pyridine nitrogen, electrostatic reason might be responsible for that limit:

the formation of a twice negatively charged fourth complex may be disfavoured in pyridine with its low dielectricity constant

($\epsilon=12.3$), while fourth complexes even with thiolate anions have been isolated as solids from solvents with higher dielectricity constants [38,42,66-69].

Only one cationic complex, " $(\text{HgS}^{\text{n}}\text{Bu})^+$ ", was investigated. It has been noted in the previous section that the solubility is lower for the cationic than for the anionic complexes. The experimental material allows the decision that a dimeric sulfur bridged complex $[\text{Hg}_2(\text{S}^{\text{n}}\text{C}_4\text{Hg})_2]^{2+}$ is formed. The distances mercury-mercury and mercury-sulfur were refined and obtained to 369 and 249 pm, respectively. A sulfur bridged chain structure, which is observed in solids of the same thiolate-mercury ratio [26-28], would also have explained the positions of the main peaks in the electric RDF, but not their relative intensities (see [VI]).

Even in the case of this dimer it is likely that several pyridine molecules coordinate to the mercury(II) ions and thus complete the mercury environment to a distorted tetrahedral or octahedral coordination sphere.

For none of the systems, however, any refinement was possible for this solvation of mercury(II) by pyridine molecules. The coordination of pyridine molecules to the mercury ions is likely for all three systems, but the raw data are not of sufficient quality to prove and characterize this solvation.

3.1.3. Crystal Structures

3.1.3.1. General Points of View

It has been stated initially that the structures of a number of solid mercury(II) thiolates complexes have been reported in the literature. So far, however, no good compilation for these compounds has been undertaken. The most important of these structures were therefore briefly described, and essential interatomic distances have been given in Table I. In order to complete the material which was found in the literature, the crystal structures of the following mercury(II) thiolate complexes were solved:

[I] acetato(benzenethiolato)mercury(II), $[\text{HgSPh}]_2\text{O}_2\text{CCH}_3$;

[II] di(1-butanethiolato)mercury(II), $\text{Hg}(\text{S}^{\text{n}}\text{C}_4\text{Hg})_2$.

The important distances in these compounds were included in Table I at suitable places.

3.1.3.2. The Crystal Structure of Acetato(benzenethiolato)-mercury(II)

For selected interatomic distances and bond angles see Table 2 in [I]. The solid is built up from parallel, folded, cis-trans type (-Hg-SPh-) chains (Fig.1 in [I]) linked to sheets (Fig. 2 in [I]) by acetate bridges. Two independent mercury atoms Hg(1) and Hg(2) with two different environments are found in the structure. The mercury atom Hg(1) is coordinated by two bridging sulfur atoms almost linearly; four oxygen atoms from three different acetate ions complete its coordination sphere to a distorted octahedron. Only three oxygen atoms, from two different acetate ions, and two bridging sulfur atoms coordinate the mercury atom Hg(2); the S-Hg(2)-S array is strongly bent. The coordination sphere of the Hg(2) atom is so irregular that it can not easily be derived from a regular polyhedron by distortion. It is suggested that the two S-atoms, together with the O3 oxygen atom, form the equatorial plane in a strongly distorted pentagonal bipyramid, the oxygen atoms O4 and O3^{iv} occupy its "axial" positions (see Table 2). Similar chain structures, but less folded and of all-trans type, are formed in the closely related compounds [HgSR]O₂CCH₃ (R=Me, ⁿC₃H₇, ⁿC₄H₉), and in their pyridine, or 4-methyl-pyridine (4-Mepy, γ-picoline) solvated analogues [HgSR]O₂CCH₃*Py (R=Me, Et) and [HgSR]O₂CCH₃*(4-Mepy) [26-28].

The compounds without organic nitrogen ligands are built up of parallel all-trans (zig-zag) chains of (-Hg-RS-), with atoms, linked to sheets via bridging acetate ions in nearly the same way as in the title compound [26,27].

In the compounds with N-donor molecules, the same type of chains is formed, but they are isolated and do not combine to sheets since important coordination sites at the mercury ions are occupied by the nitrogen ligands [26,28].

For more details see [I], for comparisons see Table I.

3.1.3.3. The Crystal Structure of Di-1-butanethiolatomercury(II) at 207K

For selected interatomic distances, and bond angles, see Table 2 in [II].

The structure may be described as a system of tubes built up by parallel helices composed of chains of linked $\text{Hg}(\text{S}^{\text{n}}\text{C}_4\text{H}_9)_4$ tetrahedra. All sulfur atoms are bridging and the two independent mercury atoms are four coordinated with a distorted tetrahedral environment, (see Fig.1 in [II]). Two types of HgS_4 tetrahedra occur; those which are connected to four neighbour tetrahedra by sharing corners, and those sharing two corners with two neighbours, and one edge with a third neighbour. Both types of linkage between the tetrahedra can clearly be seen in Fig. 2 in [II], where a projection of the chains of tetrahedra on the ab-plane is shown. For greater clarity the hydrocarbon groups have been omitted in that figure.

The chains form helices, running parallel to c and linked to each other by sharing eight tetrahedra for one unit cell translation c, two tetrahedra on either side of a basic quadrangle with the side length of $a/2$.

A characteristic property of this type of helices being dependent of each other due to sharing parts of the structural elements, is that if one of the helices turns clockwise around the c-axis, its closest neighbour helices will turn counterclockwise along the same axis, and vice versa.

One closely related structure has been reported by Kunchur [36]. He found that solid di-t-butylthiolatomercury(II) is also built up by $\text{Hg}(\text{SR})_4$ tetrahedra linked together by sulfur bridges. The difference is, however, that in the latter compound all tetrahedra are linked together by sharing opposite edges, thus straight chains are produced, and no spatial structure is observed.

For comparisons see Table I, there the structure of the title compound is included at a suitable place.

The tubes which are formed by the mercury-sulfur helices are filled with the hydrocarbon group bonded to the sulfur atoms.

For more details see [II].

It was necessary to collect the raw data at low temperature (-65°C). Probably the distances calculated from this data set are somewhat smaller than what they might be in the compound at room temperature.

3.1.4 Some General Remarks about Coordination Chemistry of Mercury(II) Thiolate Derivates

In solids sulfur bridges are often formed when the ligand-mercury ratio is two or lower. In the cases of formal 1:1 complexes, and for at least two 2:1 complexes, polymeric structures were found. But even in the "molecular" 2:1 complexes $\text{Hg}(\text{SR})_2$ ($\text{R}=\text{Me}, \text{Et}$) with their linear two-coordination of the mercury ions by close thiolate anions, a higher coordination number of the metal is found, if the three or four sulfur atoms which coordinate to the mercury atoms equatorially at long distances, and complete their coordination sphere to a distorted square pyramide or octahedron, are taken into account.

Then these sulfur atoms must be regarded as bridges, and the structure as some kind of a three dimensional polymer (see Table I and refs therein).

Even for a ligand-metal ratio of three one such example is found [38]. The $(\text{NEt}_4)_2[\text{Hg}_2(\text{SMe})_6]$ contains a dimer of two distorted $\text{Hg}(\text{SMe})_4$ tetrahedra linked together via sulfur bridges by sharing an edge.

On the other hand, completely isolated mononuclear mercury(II) thiolate complexes were found in a few solids. One of them is the tris(benzenethiolato)mercurate(II) anion which is trigonally planar and was found in $[\text{NEt}_4][\text{Hg}(\text{SPh})_3]$ [40]. The other example is the tetrakis(4-chlorobenzenethiolato)mercurate(II) dianion which is a slightly distorted tetrahedron and has been found in the $(\text{Me}_4\text{N})_2[\text{Hg}(\text{SC}_6\text{H}_4\text{Cl})_4]$ [42].

In dilute pyridine solution mononuclear complexes between thiolate anions and the mercury(II) acceptor were formed. No tendency towards oligomerisation or polymerisation was stated in this concentration range. In the concentration range close to saturation, however, the $\text{Hg}(\text{S}^{\text{N}}\text{C}_4\text{H}_9)^+$ ion was found to form a dimer. The $[\text{Hg}(\text{SR})_3]^-$ complexes were monomeric even at high concentrations. This shows the same tendency as in the solid state; the monomer of higher complexes can exist under certain conditions, while the first complex can be mononuclear only if the coordinating power and the activity of the solvent is sufficiently high. Pyridine seems to fulfill these conditions in dilute solutions; at higher complex concentrations it is not able to suppress the formation of sulfur bridges completely, and the dimeric cations are formed. This is nothing else than the initial step of polymerisation to chains as they are well known from the solids.

3.2 Mercury and Neutral Sulfur, Selenium, and Tellurium Ligands

3.2.1. The Complex Formation between Mercury(II) Compounds and the Cyclic Ligands THT, THSe and THTe

Efforts to determine the complex formation constants between mercury(II) and THT and two other thioethers in pyridine and DMSO solution with the same methods as for the thiols and thiolates were not successful [V]. If there was any complex formation in these solvents, the equilibrium constants are of an order of magnitude that they are not obtainable with neither potentiometric nor calorimetric methods.

Since thioethers are well known to form complexes with mercury(II) compounds in solvents with lower donicity, like water and alcohols [9,15,16,18-22,43-45,48-51,56,70,71], it was reasonable to check the ability of the thioethers which had been applied to mercury with another metal acceptor in the same solvent system. Silver (I) was chosen for that purpose.

Formation of one weak silver(I) complex was observed with diphenylsulfide in DMSO and with THT in pyridine, while the formation of two weak complexes was found with THT in DMSO [V]. Since it is known that mercury(II) and silver(I) are very similar in their properties as metal acceptors, it is allowed to draw the conclusion that even mercury(II) might form one or two weak THT complexes in DMSO, perhaps even in pyridine. Unfortunately this complex formation, if it occurs, is out of the limits of detection.

For this reason no efforts of potentiometric or calorimetric titration were undertaken on the THSe and THTe ligands, but the approach was changed. The solid complexes of mercury(II) perchlorate and halides with the THSe and THTe ligand, and of the mercury(II) perchlorate with THT, were prepared and examined with vibration spectroscopy [VII]. In three cases, $\text{Hg}(\text{THSe})\text{Cl}_2$ and $\text{Hg}(\text{THSe})_2\text{X}_2$; $\text{X}=\text{Br}, \text{I}$, single crystals were obtained and the structures of these compounds determined [III, IV].

3.2.2. The Crystal Structure of Tetrahydroselenophenemercury(II) Chloride

For interatomic distances, and bond angles, see Table 2 in [III]. The compound consists of parallel double chains formed from trigonal $\text{Hg}(\text{THSe})\text{Cl}_2$ units by halogene bridging (Fig.1 in [III]). The halogene bridges are formed in such a way that half of the chloride ions coordinate to only one mercury atom at a short distance (235.3 pm), while the other half of the chloride ions coordinate to three mercury ions at three different distances (263.4 pm; 284.2 pm; 316.5 pm), thus linking the trigonal units to a double string chain. The THSe molecules coordinate to the mercury ions without forming bridges, thus the environment around each mercury ion can be described as a distorted trigonal bipyramid, with the THSe, one terminal, and one bridging chloride ion in the equatorial plane, and with the two most distant

chloride ions in the axial positions. For more details, especially for distances and angles within the THSe molecules, see [III] . The structure type found in $\text{Hg}(\text{THSe})\text{Cl}_2$ is rare, but not unique. Brändén [18,48] reported the crystal structure of the corresponding THT complex, and the two compounds are isomorphous. One more compound with the same type of mercury(II) chloride double string chain is the $\text{Hg}(\text{PMe}_3)\text{Cl}_2$; the structure was reported by Bell et.al. [72] and by Jones [52]. The corresponding distances in these two analogous compounds were included in Table III in [VII] together with those from the title compound.

3.2.3. The Crystal Structures of Dibromobis(tetrahydroselenophene)-mercury(II) and Diiodobis(tetrahydroselenophene)mercury(II)

The structures of both compounds are built up in the same way and can be treated together. Anyhow, the compounds are not isomorphous, and the similarity concerns mainly the chemical type of interaction and not so much the crystallographic aspects. Both compounds are built up of simple, isolated, monomeric pseudotetrahedral molecules $\text{Hg}(\text{THSe})_2\text{X}_2$ ($\text{X}=\text{Br}, \text{I}$) of approximately C_{2v} point group symmetry.

It should, however, be mentioned that two slightly crystallographically independent tetrahedra occur in the iodide, while all tetrahedra are of the same type in the bromide. The two slightly different distortions in the iodide structure are probably caused by packing effects. For intramolecular distances, and bond angles, see Table 3 in [IV].

Recently the structures of the analogous compounds $\text{Hg}(\text{THT})_2\text{X}_2$ with $\text{X}=\text{Cl}, \text{Br}$ were solved [49], and some of the distances in one of these compounds ($\text{X}=\text{Br}$) were included in Table [IV] in [VII], together with some distances in the title compounds. The molecular structures are very similar. One of the two $\text{Hg}(\text{THSe})_2\text{I}_2$ molecules is shown in Fig.2 [VII], and the $\text{Hg}(\text{THSe})_2\text{Br}_2$ molecule and the packing of the $\text{Hg}(\text{THSe})_2\text{I}_2$ molecules in the unit cell are drawn in [IV].

3.2.4. Vibrational Spectroscopy

The Raman and IR spectra of the solid complexes formed from mercury(II) halides, and perchlorate, with THSe and THTe are reported in the wavenumber region below 750 cm^{-1} (Table II in [VII]). Assignments have been based on literature for internal ligand modes [53], for mercury(II) halide modes [16,50-52,72-99], and for the modes of the perchlorate ion [100].

In the case of the mercury(II) halide THSe complexes the assignments were based on the structural data which are reported in [III] and [IV]. In order to complete and systematize the spectroscopic data material, the mercury(II) perchlorate THT complex was prepared and investigated by IR and Raman spectroscopy.

Moreover, a Raman spectrum was recorded of the well known compound $\text{Hg}(\text{THT})\text{Cl}_2$, since it was missing in the previous works [51,52]. The aim of this spectroscopic investigation was to systematize the single observations, to find a correlation between structure and vibrational spectra, and thus to suggest possible structures for the solid mercury(II) halide THTe complexes there single crystals were not obtained.

All assignments in Tables II-IV in paper [VII] are tentative. No final decision is so far possible for e. g. assignments of the mercury-ligand stretching modes for the mercury(II) halide THSe and THTe complexes. On that reason the mercury halide vibrations were assigned first according to examples from the literature [16,52,72-99], and hence it was discussed which of the left-over bands might belong to the Hg-L stretching modes.

It becomes obvious from Table III in [VII] that the similarity in the structure of HgLCl_2 ($\text{L}=\text{THT}, \text{THSe}, \text{PMe}_3$) results in a similarity of the nonligand vibrations, too. In all three compounds the stretching vibrations along the shortest Hg-Cl bond can be assigned to bands around 300 cm^{-1} . The stretching modes of the longer Hg-Cl contacts can be assigned to bands in the region $197-115\text{ cm}^{-1}$.

In Table IV in [VII] the same is shown for the L_2HgX_2 ($\text{X}=\text{Br}, \text{I}$)

complexes with pseudotetrahedral molecular structure. Here the Hg-Br and Hg-I stretching vibrations are assigned, following similar examples from the literature, to bands at 158 cm^{-1} (Ra) for the bromide and at 145 and 125 cm^{-1} (Ra) for the iodide. Hg-Se stretching vibrations were assigned to bands at 237 cm^{-1} (Ra) in $\text{Hg}(\text{THSe})\text{Cl}_2$ and at 196 cm^{-1} (IR,Ra) and 215 cm^{-1} (IR) in $\text{Hg}(\text{THSe})_2\text{Br}_2$, according to literature assignments [98,99]. In the perchlorates the Hg-Se stretching modes were found at 134 cm^{-1} in $[\text{Hg}(\text{THSe})_3]\text{ClO}_4)_2$ and at 158 cm^{-1} in the hypothetical " $[\text{Hg}(\text{THSe})_2](\text{ClO}_4)_2$ ". For further explanations see [VII]. It is remarkable that no band was observed in the Raman spectrum of $\text{Hg}(\text{THSe})\text{I}$ in the region $300\text{--}150\text{ cm}^{-1}$. No assignment could therefore be suggested for the Hg-ligand mode. In the THTe complexes $\text{Hg}(\text{THTe})\text{X}_2$ ($\text{X}=\text{Cl},\text{Br}$) the mercury-halide stretching modes were assigned to bands at 277 cm^{-1} (Ra) and 288 cm^{-1} (IR) for the chloride and at 185 cm^{-1} (Ra) and 189 cm^{-1} (IR) for the bromide, respectively. For bands and assignments in the lower wavenumber region see Table II and text in [VII]. The Hg-Te vibrations can be assigned either to the strong Raman bands at 146 cm^{-1} in the chloride and at 134 cm^{-1} in the bromide, or to the bands at 123 cm^{-1} (Ra) in the chloride and at about 125 cm^{-1} (IR) in the bromide [92,99]. In $[\text{Hg}(\text{THTe})_4](\text{ClO}_4)_2$, however, the Hg-Te vibrations are found at 112 cm^{-1} (IR,Ra) and 101 cm^{-1} (Ra), respectively. Unfortunately the spectroscopic material is still too poor to allow the final decision whether the selenium or the tellurium ligand is the better donor towards the mercury(II) ion. In this context a work recently published by Konovalov and Davarsky [97] is useful for the interpretation of some of the data. According to their results there is a correlation between the wavenumber position of the antisymmetric stretching vibration ν_{as} (X-Hg-X), or the stretching vibration $\nu(\text{Hg-X})$ if only one halogen X is present, and the length of the Hg-X interaction. For greater clarity some examples for this correlation have been collected in Table II.

TABLE II: Interatomic Distances $r(\text{Hg-Cl})$ and Stretching Vibrations (Hg-Cl) for Some Complexes between Mercury(II) Chloride and Selected Organic Ligands (after 97).

Raman values are given in italics as far as specified in literature.

Complex	$r(\text{Hg-Cl})$ in pm	Ref.	(Hg-Cl) in cm^{-1}	Ref.
$(\text{Me}_2\text{SO})_2(\text{HgCl}_2)_3$	230.6, 230.9	101a	345, 291	101a
	232.0		339, 288 ^a	
	300.4			
	308.1			
$(\text{Ph}_2\text{SO})\text{HgCl}_2$	228.9, 229.1	101b	362, 311 (308)	101b
	2*323			
	2*328			
$(^n\text{Bu}_2\text{SO})\text{HgCl}_2$	233	102	348	102
	235		304 (298) ^a	
	313			
	316			
	233	103	310	103
$(\text{H}_5\text{C}_5\text{NO})_2\text{HgCl}_2$ (Quinoline-N-oxide) HgCl_2	2*230	104	349, 344, 334, 313, 298,	52
			290, 281	
	312			
$(\text{Coumarin})\text{HgCl}_2$	335			
	2*229	105	349	52
	294			
	323			
	328			
$(\text{H}_5\text{C}_5\text{N})_2\text{HgCl}_2$ HgCl_2 in pyridine solution	4*275.4	106	146 (148)	85, 107
	2*237.5	94	313, 287 (282)	94

TABLE II: (cont inued)

(2,4,6-Trimethylpyridine)HgCl ₂	254,258 295,296	108	261,229	52
(9-Methylhypoxanthine-N7)HgCl ₂	235.4 240.1	86	325 275(276) ^a	86
(MPC)HgCl ₂ ^b	237 257 278	109	291 206 132	52
(Et ₂ S)(HgCl ₂) ₂	230,233 235,241 270-364	110	342 311	101a
(Thiourea) ₂ HgCl ₂	2*257 322	111	215 119 ^c	112
(THT)HgCl ₂	230 262 283 307	48	322,312(311) 197(195) 164(170) ^a 134,124 ^a	52,VII
(THSe)HgCl ₂	235.5 263.4 284.2 316.5	III	307(305) ^a 188(189) ^a (159) ^a (141,129) ^a	VII
(Me ₃ P)HgCl ₂	235.5 278.2 294.1 348.9	52,72	300(291) 141(142) ^a	52

TABLE II: (continued)

(Ph ₃ P)HgCl ₂	237.0	52, 72, 113	291, 288 (186)	52, 72, 113
	262.3		188	
	265.8		183	
(1, 2, 5-Triphenylphosphole)HgCl ₂	240.4	52, 72, 113	283 (278)	52, 72, 113
	254.2		219 (204)	
	274.7		168 (168), 158	
(Et ₃ P)HgCl ₂	242	52, 72	286 (270, 260)	52
	256		203 (207), 198	
	304		117 (126) ^a	
	321		105 ^a	
(ⁿ Bu ₃ P)HgCl ₂ (-form)	234.8	52, 91	301, 295 (298)	52, 91
	272.0		173 (177)	
	273.6		150 (148)	

^a own assignments. ^b MPC= methylpyrrolidine-1-carbodithioate.

^c assignment by Konovalov & Davarski [97].

This table contains only data on mercury(II) chloride complexes with organic ligands, and consists to one part of parts of the Table 1 in [97], but was extended with data from more recent literature, and with own results from [III], [IV] and [VII].

Similar correlations between bond lengths and stretching vibration frequencies have been stated to exist even for the Hg-Br and Hg-I interaction [52,97]. There are, however, fewer examples accessible from previous literature, and on that reason the comparably well known Hg-Cl interaction was chosen for Table II. As is seen in the Table, the results from [III], [IV] and [VII] fit well to the results from previous works.

3.3. Summary and Remarks

The complex formation between mercury(II) and 1-butanethiolate and thiophenolate anions in dilute pyridine solution yields three mononuclear complexes $[\text{Hg}(\text{SR})_x]^{2-x}$ ($x=1-3$). Similar observations have been previously reported for complex formation between mercury(II) and thiocyanate in the same solvent [60].

The same complexes are formed whether the sodium thiolates, or the free RSH, were used as ligand. An explanation for this behaviour is given. All complex-formation steps are exothermic.

Structures in concentrated pyridine solution were determined with X-ray scattering methods. The two anionic complexes $[\text{Hg}(\text{SR})_3]^-$ are trigonal-planar and mononuclear. It is therefore assumed that they have the same structure in dilute solution. Axial pyridine coordination to mercury is suggested, but can be neither proved nor excluded.

The structure of the cationic complex " $\text{HgS}^{\text{II}}\text{C}_4\text{H}_9^+$ " in concentrated pyridine is surprising. The complex is a flat, tetragonal dimer. There are, however, no indications for the presence of dimers in dilute pyridine solutions no dimers were found. An explanation for this surprising behaviour is given.

The crystal structures of $[\text{HgSC}_6\text{H}_5]\text{O}_2\text{CCH}_3$ and $\text{Hg}(\text{S}^n\text{C}_4\text{H}_9)_2$ were determined. They are similar to structures of related compounds reported in literature [26-42]. From the structural data on the complexes in solution and in the solid state, the tendency to medium coordination number (CN=2-5) between mercury(II) and thiolate, and other mercaptide, ligands is pointed out (Table I). The crystal structures of the complexes between the cyclic selenoether tetrahydroselenophene (THSe) and the three mercury halides HgX_2 (X=Cl, Br, I) were determined. They are similar to structures of mercury(II) halide complexes with other strong, soft type organic donors, like thioethers and phosphines. The vibrational spectra of the complexes of the mercury(II) halides, and perchlorate, with THSe and the corresponding cyclic telluroether were recorded. Assignments for the mercury-halide stretching vibration are in good agreement with those in literature. The mercury-ligand stretching vibrations are more difficult to assign and are, except in the perchlorates, still unsure. A final decision whether the selenium or the tellurium ligand is the better donor towards the mercury(II) acceptors can therefore not be derived from these results.

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Table III: Selected Structural and Spectroscopic Data on a Series of Isostructural 1:1 Complexes of Mercury(II) Chloride. Values from Raman measurements are in italics. The atom numbering is the same as in Fig. 1 and in [50].

Complex:	Hg(SC ₄ H ₈)Cl ₂	Hg(SeC ₄ H ₈)Cl ₂	Hg(PMe ₃)Cl ₂
distances (pm)			
Hg-L	240 ^{<u>d</u>}	253.5 ^{<u>b</u>}	236.5 ^{<u>c</u>}
Hg-Cl ₂	230 ^{<u>d</u>}	235.5 ^{<u>b</u>}	235.5 ^{<u>c</u>}
Hg-Cl ₁	262 ^{<u>d</u>}	263.4 ^{<u>b</u>}	278.2 ^{<u>c</u>}
Hg-Cl ₁ ⁱ	307 ^{<u>d</u>}	316.5 ^{<u>b</u>}	348.9 ^{<u>c</u>}
Hg-Cl ₁ ⁱⁱ	283 ^{<u>d</u>}	284.2 ^{<u>b</u>}	294.1 ^{<u>c</u>}
stretching vibrations (cm ⁻¹)			
Hg-L	279 (277) ^{<u>d</u>}	(237) ^{<u>e</u>}	361 (363) ^{<u>f</u>}
Hg-Cl ₂	322, 312 (311) ^{<u>d</u>}	307 (305) ^{<u>e</u>}	300 (291) ^{<u>f</u>}
Hg-Cl ₁	197 (195) ^{<u>d</u>}	188 (189) ^{<u>e</u>}	
Hg-Cl ₁ ⁱ g	134, 124 ^{<u>d</u>}	(141), (129) ^{<u>e</u>}	
Hg-Cl ₁ ⁱⁱ	164 (170) ^{<u>d</u>}	(159) ^{<u>e</u>}	141 (142) ^{<u>f</u>}

^a from [29], ^b from [50], ^c from [49] and [56]

^d IRdata from [49] Raman data: this work, ^e this work

^f from [49] ^g for tentative assignments in the low wavenumber see in the text.

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Structure of Acetato(benzenethiolato)mercury(II)

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Abstract. $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_6\text{H}_5\text{S})$, $M_r = 368.80$, monoclinic, $P2_1/n$, $a = 18.362(2)$, $b = 7.485(1)$, $c = 14.292(2)$ Å, $\beta = 104.72(1)^\circ$, $v = 1900.0(3)$ Å³, $Z = 8$, $D_x = 2.58 \text{ g cm}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.71069$ Å, $\mu = 164 \text{ cm}^{-1}$, $F(000) = 1344$, $T = 295 \text{ K}$, $R = 0.034$ for 2326 unique observed reflections. The structure is built up of infinite -S-Hg-S- chains linked via acetate groups to sheets. The two independent Hg-atoms, five- and six-coordinated, are besides the two thiolate groups also bonded to two and three acetate ligands, respectively.

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Introduction. It has for a long time been known that mercury(II) forms extremely stable, water insoluble compounds with organic sulfur ligands of types thioalcohols RSH ($R = \text{Alk, Ar}$). Solid complexes between these thiols and Hg(II) have been isolated with thiol/mercury ratios (Th/Hg) varying from 1 to 4. Many of these complexes have been the subject of intense spectroscopic investigations and the crystal structures of some of them have been determined. For Th/Hg ratios 3 or 4, mostly thiophenols have been used as ligands e.g. by Christou, Foltling & Huffman (1984) and Choudhury, Dance, Guernsey & Rae (1983). For structure determinations of the neutral compounds $\text{Hg}(\text{SR})_2$ and for the 1:1 complexes $\text{Hg}(\text{SR})\text{X}$, however, alkyl thiols have so far been preferred as ligands, e.g. by Wells (1937), Bradley & Kunchur (1963, 1964), Kunchur (1964), Taylor & Carty (1977), Perchard et al. (1981), Perchard, Baron & Loze (1984), Barrera et al (1982), Biscarini, Foresti & Pradella (1984), Canty, Raston & White (1978, 1979a,b), Johansson (1939) and Puff, Sievers & Elsner (1975). The crystal structures of the 1:1 complexes so far studied (Canty, Raston, & White, 1979a) have been found to be dependent on the donicity of the anion X; the chloride, bromide and acetate anions have earlier been used. In this study acetate and thiophenolate anions were chosen to allow a direct comparison with the results given in the previous work.

Experimental. Crystals grown from an acetonitrile solution of mercury acetate and mercurythiophenolate. Plate-shaped transparent crystal, 0.25x0.20x0.09 mm, CAD-4 diffractometer, graphite-monochromatized MoK radiation, variable-speed, ω -2 θ scans, width $(0.80+0.60 \tan\theta)^\circ$, max. recording time 150 s. Three standard reflections, no significant variations. Lattice parameters based on 40 diffractometer θ values. 3585 reflections, $\theta \leq 25^\circ$, $0 \leq h \leq 17$, $0 \leq k \leq 7$, $-13 \leq l \leq 13$, 2327 with $I > 3\sigma(I)$. Lp and absorption corrections, transmission factors 0.06-0.22. Structure solved by direct methods with MULTAN80 (Main et al., 1980). Full-matrix least-squares refinements minimizing $\Sigma w(\Delta F)^2$, $w = [\sigma^2(F_o) + (0.030 \cdot F_o)^2 + 2.5]^{-1}$, anisotropic temperature factors for non-C atoms and phenyl-H atoms included with fixed parameters in calculated positions ($d(C-H) = 1.00 \text{ \AA}$). Final refinement with 2326 reflections, 138 variables, $R = 0.034$, $wR = 0.041$, $S = 1.0$. Corrections for secondary extinction (Zachariasen, 1967) $g = 0.19(2) \times 10^{-4}$. $(\Delta/\sigma)_{\max} = 0.02$, final $\Delta\rho$ excursions $\leq |1.3| \text{ e \AA}^{-3}$. Scattering factors and anomalous dispersion factors from International Tables for X-ray Crystallography (1974). Program used: see Lundgren (1982).

Discussion. Final atomic coordinates and temperature factors are listed in Table 1* and selected interatomic distances and angles in Table 2. The present structure may be described as built up of endless $(-\text{Hg}-\text{SR}-)_n$ chains running in the y direction, linked via the acetate groups to sheets parallel to [101]. Infinite chains with Hg diagonally coordinated by O or S atoms are building elements of many mercury(II) structures. The chains can be either planar or spiral, the latter found in the trigonal forms of HgO and HgS. The planar chains are of two types, +- or overall trans chains as found in the orthorhombic HgO (Aurivillius, 1965a) and +-+ or alternating cis-trans chains originally found in $\text{Hg}(\text{OHg})_4\text{Br}_2$ (Aurivillius, 1965b) but later on also in $\text{Hg}_3\text{S}_2\text{Cl}_2$ (Aurivillius, 1967).

Previous studies of 1:1 mercury thiolate complexes of type RSHgX with $\text{X} =$ acetate have shown the presence of $(-\text{Hg}-\text{SR}-)_n$ chains (Canty, Raston & White, 1979a) often crosslinked by weakly bonded (Hg-O 2.70-2.86 Å) acetate groups (Puff, Sievers & Elsner, 1975; Canty, Raston & White, 1979a). If the compounds with R = methyl and ethyl are crystallized from pyridine, 1:1 adducts are obtained, containing isolated chains with pyridine and acetate coordination at each mercury (Canty, Raston & White, 1978, 1979a). All chains are infinite and of the overall trans type with considerable deviations in the S-Hg-S and Hg-S-Hg angles from the ideal values of 180 and 109°.

*List of structure factors, anisotropic thermal parameters and phenyl-H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No SUP ...

In the present study the chains are of the cis-trans type with angles at the Hg and S atoms of 162.4, 143.7 and 98.1, 98.4° and with Hg-S distances in the range 2.403-2.481 Å (Table 2). The two independent Hg atoms are, besides to the thiolate groups, also bidentate coordinated to one acetate group with Hg-O bonds in the range 2.38-2.55 Å. Hg(2) is further bonded to one acetate ligand and Hg(1) weakly bonded to two (Table 2, Fig. 1). These acetate groups link Hg(1) atoms within one chain (Hg(1)-O 2.85, 2.87 Å), while the acetate groups bonded to Hg(2) form double-bridges (Hg(2)-O 2.55, 2.57 Å), crosslinking the chains into layers (Fig. 2). Distances and angles within the acetate and thiolate ligands are unexceptional.

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Table 1. Atomic coordinates and isotropic temperature factors ($\text{\AA}^2$)

$$U_{eq} = \frac{1}{3} \sum_{i,j} U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x/a	y/b	z/c	Uiso/ Ueq
Hg1	0.22966(2)	0.27218(6)	0.78315(3)	0.0372(2)
Hg2	0.11076(2)	0.03241(6)	0.57394(3)	0.0389(2)
S1	0.10624(15)	0.29901(36)	0.67547(19)	0.0359(9)
S2	0.33096(14)	0.23898(37)	0.92707(20)	0.0367(9)
O1	0.3139(5)	0.4126(12)	0.6931(6)	0.0563(34)
O2	0.2847(5)	0.1336(11)	0.6562(6)	0.0519(31)
O3	0.0156(4)	0.1238(12)	0.4360(6)	0.0532(31)
O4	0.1273(4)	0.1907(13)	0.4226(7)	0.0663(37)
C11	0.0439(6)	0.2476(14)	0.7496(7)	0.034(2)
C12	0.0666(7)	0.2466(17)	0.8495(10)	0.056(3)
C13	0.0144(8)	0.2185(20)	0.9032(11)	0.066(4)
C14	-0.0595(8)	0.1852(19)	0.8572(11)	0.063(4)
C15	-0.0823(7)	0.1892(18)	0.7584(10)	0.055(3)
C16	-0.0316(6)	0.2177(16)	0.7040(9)	0.044(3)
C21	0.2818(6)	0.2328(14)	1.0194(8)	0.035(2)
C22	0.2435(6)	0.3779(16)	1.0444(8)	0.045(3)
C23	0.2038(7)	0.3603(19)	1.1138(10)	0.059(3)
C24	0.2045(8)	0.1965(20)	1.1613(11)	0.065(4)
C25	0.2428(8)	0.0581(19)	1.1383(10)	0.061(4)
C26	0.2809(7)	0.0690(17)	1.0671(9)	0.050(3)
C31	0.3182(6)	0.2731(14)	0.6461(8)	0.035(2)
C32	0.3663(8)	0.2767(18)	0.5736(10)	0.060(3)
C41	0.0572(7)	0.1952(17)	0.3883(9)	0.051(3)
C42	0.0232(9)	0.2823(21)	0.2913(12)	0.076(4)

Table 2. Selected bond lengths (Å) and angles (°)

In the coordination spheres of the Hg atoms

Hg(1)-S(1)	2.403(3)	Hg(2)-O(3)	2.378(8)
Hg(1)-S(2)	2.410(3)	Hg(2)-S(2 ⁱⁱⁱ)	2.445(3)
Hg(1)-O(1)	2.483(9)	Hg(2)-S(1)	2.481(3)
Hg(1)-O(2)	2.514(8)	Hg(2)-O(4)	2.551(10)
Hg(1)-O(1 ⁱ)	2.852(9)	Hg(2)-O(3 ^{iv})	2.569(8)
Hg(1)-O(2 ⁱⁱ)	2.873(8)		
S(1)-Hg(1)-S(2)	162.4(1)	S(1)-Hg(2)-S(2 ⁱⁱⁱ)	143.7(1)
S(1)-Hg(1)-O(1)	104.1(2)	S(1)-Hg(2)-O(3)	97.3(2)
S(1)-Hg(1)-O(2)	93.4(2)	S(1)-Hg(2)-O(3 ^{iv})	103.6(2)
S(2)-Hg(1)-O(1)	92.2(2)	S(1)-Hg(2)-O(4)	98.7(2)
S(2)-Hg(1)-O(2)	102.1(2)	S(2 ⁱⁱⁱ)-Hg(2)-O(3)	119.0(2)
O(1)-Hg(1)-O(2)	51.9(3)	S(2 ⁱⁱⁱ)-Hg(2)-O(3)	88.9(2)
Hg(1)-S(1)-Hg(2)	98.1(1)	S(2 ⁱⁱⁱ)-Hg(2)-O(4)	105.4(2)
Hg(1)-S(2)-Hg(2 ⁱⁱ)	98.4(1)	O(3)-Hg(2)-O(3 ^{iv})	67.8(3)
		O(3)-Hg(2)-O(4)	52.0(3)
		O(3 ^{iv})-Hg(2)-O(4)	117.7(3)

Symmetry code: (i) $1/2-x, -1/2+y, 11/2-z$; (ii) $1/2-x, 1/2+y, 11/2-z$;
 (iii) $1/2-x, -1/2+y, 11/2-z$; (iv) $-x, -y, 1-z$

Table 2. continued

In the thiolate ligands

S(1)-C(11)	1.79(1)	S(2)-C(21)	1.78(1)
C(11)-C(12)	1.38(2)	C(21)-C(22)	1.39(2)
C(12)-C(13)	1.39(2)	C(22)-C(23)	1.38(2)
C(13)-C(14)	1.37(2)	C(23)-C(24)	1.40(2)
C(14)-C(15)	1.37(2)	C(24)-C(25)	1.34(2)
C(15)-C(16)	1.37(2)	C(25)-C(26)	1.38(2)
C(16)-C(11)	1.39(2)	C(26)-C(21)	1.41(2)
S(1)-C(11)-C(12)	122.9(8)	S(2)-C(21)-C(22)	123.8(8)
S(1)-C(11)-C(16)	118.0(8)	S(2)-C(21)-C(26)	117.0(8)
C(12)-C(11)-C(16)	119(1)	C(22)-C(21)-C(26)	119(1)
C(11)-C(12)-C(13)	120(1)	C(21)-C(22)-C(23)	120(1)
C(12)-C(13)-C(14)	120(1)	C(22)-C(23)-C(24)	119(1)
C(13)-C(14)-C(15)	120(1)	C(23)-C(24)-C(25)	120(1)
C(14)-C(15)-C(16)	121(1)	C(24)-C(25)-C(26)	122(1)
C(15)-C(16)-C(11)	120(1)	C(25)-C(26)-C(21)	119(1)

In the acetate ligands

C(31)-O(1)	1.255(14)	C(41)-O(3)	1.265(15)
C(31)-O(2)	1.239(13)	C(41)-O(4)	1.257(15)
C(31)-C(41)	1.523(18)	C(41)-C(42)	1.515(21)
O(1)-C(31)-O(2)	122.6(10)	O(3)-C(41)-O(4)	118.6(12)
C(32)-C(31)-O(1)	118.4(10)	C(42)-C(41)-O(3)	120.7(12)
C(32)-C(31)-O(2)	119.0(10)	C(42)-C(41)-O(4)	120.7(12)

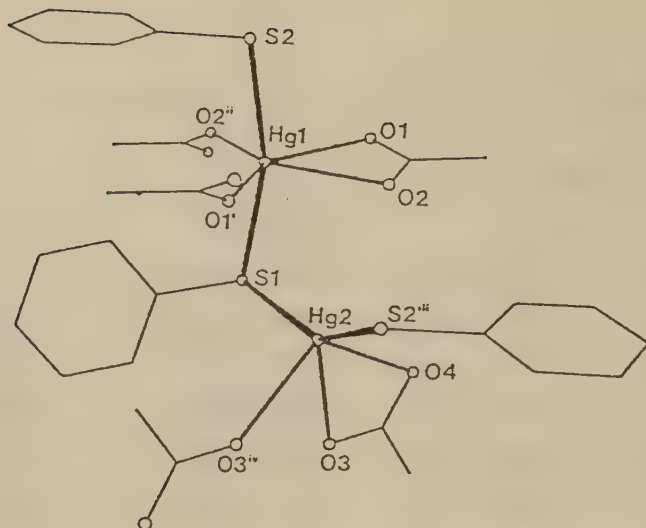


Fig. 1. The environment of the Hg atoms. Atomic numbering scheme and superscripts are given in Table 2.

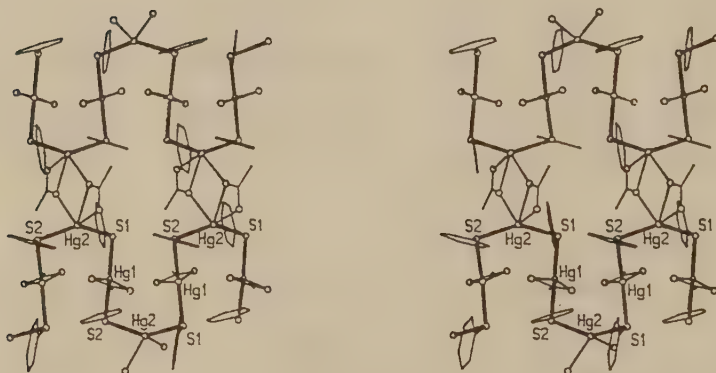


Fig. 2. Part of the layers in the structure. Infinite $(-\text{Hg-RS-})_n$ chains, running parallel to the b -axis, are linked by the acetate ligands. Hg-O bonds $> 2.8 \text{ \AA}$ are not drawn.

Structure of Bis(1-butanethiolato)mercury(II)

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Abstract. $\text{Hg}(\text{C}_4\text{H}_9\text{S})_2$, $M_r = 378.95$, tetragonal, $I4_1/a$, $a = 27.10(1)$, $c = 13.28(1)$ Å, $V = 9754(8)$ Å³, $Z = 32$, $D_x = 2.06$ g cm⁻³, $\lambda(\text{MoK}\alpha) = 0.71069$ Å, $\mu = 129$ cm⁻¹, $F(000) = 5696$, $T = 207$ K, $R = 0.036$ for 1533 unique observed reflections. The two independent Hg-atoms are tetrahedrally coordinated by the thiolate ligands. The HgS_4 tetrahedra share corners and edges forming spirals running parallel to c and with the organic residues in the cavities.

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Introduction. When Zeise (1834a,b) synthesized ethanethiol, he recognized immediately that it was the first member of a new class of compounds, closely related to alcohols, the so called thioalcohols RSH, or abbreviated thiols. He also discovered (1834c-e) their extreme affinity towards mercuric compounds to yield very stable, water-insoluble compounds $\text{Hg}(\text{SR})_2$. On these observations, he gave them a second name, mercaptanes, which he derived from the latin description of these compounds as corpora MERCURIUM CAPTANTES, i.e. the "mercury snatchers".

Immense scientific work has been laid down since those early days to describe and explain the extreme stability of the mercury-sulfur bond in this type of systems. Compounds of the simple solid neutral complex type $\text{Hg}(\text{SR})_2$ have been eagerly investigated by spectroscopy and structure determination. In the series with $\text{R} = \text{n-C}_x\text{H}_{2x+1}$ structural data were reported by Wells (1937) for the compounds with $x = 2-8$. He found that these compounds form a monoclinic isomorphous series with one exception, the $\text{Hg}(\text{SC}_4\text{H}_9)_2$ compound. In more recent works, the structures of $\text{Hg}(\text{SCH}_3)_2$ and $\text{Hg}(\text{SC}_2\text{H}_5)_2$ (Bradley & Kunchur; 1963, 1964) and of the branched compound $\text{Hg}(\text{S}^t\text{C}_4\text{H}_9)_2$ (Kunchur, 1964) have been refined. In the row $\text{Hg}(\text{SR})_2$ for unbranched alkylic groups R, structural data on the compound $\text{Hg}(\text{SC}_4\text{H}_9)_2$, that Wells pointed out as exceptional, is still missing and the purpose of this work is to complete the structural data by filling this hole.

Experimental. The compound was precipitated from an aqueous methanolic solution of mercury(II)perchlorate on addition of excess of the free thiol and single crystals were obtained by slow cooling of a warm saturated acetonitrile solution. A transparent, tetragonally bipyramidal crystal of volume $0.60 \cdot 10^{-2} \text{ mm}^3$ was enclosed in a thin-wall capillary. CAD-4 diffractometer, graphite monochromatized MoK α radiation, variable speed, ω -2 θ scans of width $(0.70 + 0.50 \tan \theta)$, max recording time 120 s. Three standard reflections, no significant variations. Lattice parameters from 25 diffractometer θ values. Cell data at 295 K, $a = 26.967(7)$, $b = 13.99(1) \text{ \AA}$, $V = 10175(7) \text{ \AA}^3$, close to data given by Wells (1937). From data collected at room temperature the Hg and S atoms were found by direct methods with MULTAN 80 (Main et al, 1980), but as refinements gave high temperature factors a new data set was collected at 207 K. Lower temperature gave broad scan peaks. Intensities of 2012 independent reflections within $\sin \theta / \lambda \leq 0.482$ ($0 \leq h, k \leq 25$, $0 \leq l \leq 12$), 1533 with $I \geq 3\sigma(I)$. Lp and absorption corrections, transmission factors 0.07-0.37. C atoms located by difference Fourier maps, full-matrix least-squares refinements, minimizing $\sum w(\Delta F)^2$, $w = [\sigma^2(F_o) + (0.035 F_o)^2 + 1.00]^{-1}$, anisotropic temperature factors for Hg and S, isotropic for C, methylene H-atoms included with fixed parameters in calculated positions ($d(\text{C-H}) = 1.00 \text{ \AA}$). One of the four organic groups was found with a disordered hydrocarbon chain and refined as two partly occupied chains. Two pairs of overlapping atoms (C41a,b; C43a, C44b) could not be resolved and were therefore included with fixed positions found from difference Fourier synthesis. Final refinement with 1533 reflections, 124 variables, $R = 0.036$, $\omega R = 0.048$, $S = 1.11$. Corrections for secondary extinction (Zachariasen, 1967) $g = 0.50(12) \cdot 10^{-4}$, $(\Delta/\sigma)_{\text{max}} = 0.03$, final $\Delta\rho$ excursions $\leq |0.75| \text{ e \AA}^{-3}$. Scattering factors and anomalous dispersion factors from International Tables for X-ray Crystallography (1974). Program used: see Lundgren (1982).

Discussion. Final atomic coordinates and temperature factors are listed in Table 1*; selected interatomic distances and bond angles are given in Table 2*. The two independent Hg atoms are both coordinated to 4 thiolate ligands (Hg-S 2.48-2.63 Å) in distorted tetrahedra (Fig. 1). The HgS_4 tetrahedra are linked by corner- and edgesharing to helical chains (Fig. 2) running parallel to $\underline{c}$. The edgesharing occurs between two Hg(1)S_4 tetrahedra. Each of the four helices in the unit cell requires 12 tetrahedra to fulfill a complete turn and shares a pair of Hg(1) tetrahedra with its four neighbouring helices. The "tubes", which are formed by the helices, are filled up by the hydrocarbon chains (not included in Fig. 2) bonded to the sulfur atoms. The structure thus exhibits a clear separation between regions of metal-chalcogene interactions and regions of only van der Waals contacts between the hydrocarbon groups. Of the four organic ligands, one has an orientationally disordered hydrocarbon chain, occupying both the normal coplanar (C41a-C44a) and a gauche (C41b-C44b) conformation. Distances and angles within the ligands are normal.

Mercury(II) usually forms complexes, which are either linear two- or tetrahedral four-coordinated. The HgS_4 tetrahedra can be isolated as found in e.g. the monomeric $\text{Hg}(\text{SC}_6\text{H}_4\text{Cl})_4$ (Choudhury, Dance, Guernsey & Rae, 1983) with Hg-S distances of 2.537-2.552 Å and as HgS_4^{6-} ions in $\text{K}_6[\text{HgS}_4]$ (Sommer & Hoppe, 1978); Hg-S 2.54-2.59 Å. Dimers and trimers of edge-sharing tetrahedra are found in $(\text{Et}_4\text{N})[\text{Hg}_2(\text{SMe})_6]$ (Bowmaker, Dance,

*Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positions together with distances and angles within the organic ligands have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP...

Dobson & Rogers, 1984) and in $(\text{PPh}_4)_2[\text{Hg}_3(\text{SCH}_2\text{CH}_2\text{S})_4]$ (Henkel, Betz & Krebs, 1985) in which the Hg-S distances vary between 2.44-2.71 Å and 2.36-2.86 Å, respectively. Chains of edge-sharing HgS_4 -tetrahedra are building element in $\text{Hg}(\text{S}^t\text{C}_4\text{H}_9)_2$ (Kunchur, 1964), in which the Hg-S distances are 2.59-2.66 Å and the S-Hg-S angles vary between 87 and 121°.

A three-dimensional network composed of both corner- and edgesharing HgS_4 tetrahedra, as found in the present structures, has earlier not been observed. Cornersharing HgS_4 tetrahedra are, however, the building elements in the zincblende structure of HgS (metacinnabarite), in which the Hg-S distances are 2.53 Å (Aurivillius, 1964, 1965).

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(1834c) J. Prakt. Chem, 1, 257-268, 396-413, 457-475.

(1834d) Pogg. Ann. 31, 369-431.

(1834e) Ann. Chim. Phys. 56, 87-96.

Table 1. Atomic coordinates and isotropic temperature factors ($\text{\AA}^2$)

$$U_{eq} = \frac{1}{3} \text{trace } U_{ij}$$

Atom	x/a	y/b	z/c	Uiso/Ueq
Hg1	0.18732(2)	0.23501(2)	0.73321(6)	0.0470(3)
Hg2	0.07009(3)	0.32023(3)	0.65616(7)	0.0543(3)
S1	0.25026(16)	0.27542(17)	0.61686(40)	0.0500(18)
S2	0.15421(15)	0.15523(16)	0.67106(40)	0.0495(18)
S3	0.13185(15)	0.30329(16)	0.79523(38)	0.0474(18)
S4	-0.01309(16)	0.31893(16)	0.74161(41)	0.0515(19)
C11	0.2301(6)	0.3399(6)	0.6225(14)	0.053(5)
C12	0.2687(8)	0.3745(7)	0.5751(17)	0.075(6)
C13	0.2504(9)	0.4287(9)	0.5766(21)	0.105(9)
C14	0.2871(13)	0.4612(12)	0.5281(28)	0.158(13)
C21	0.1910(6)	0.1427(6)	0.5602(15)	0.052(5)
C22	0.2431(7)	0.1266(7)	0.5843(15)	0.059(5)
C23	0.2747(8)	0.1143(8)	0.4947(19)	0.090(7)
C24	0.3279(9)	0.0936(9)	0.5179(20)	0.098(8)
C31	0.0920(7)	0.2755(7)	0.8911(15)	0.059(6)
C32	0.1181(10)	0.2429(9)	0.9618(21)	0.111(9)
C33	0.0871(9)	0.2225(9)	1.0447(21)	0.101(8)
C34	0.1163(17)	0.1859(15)	1.1189(35)	0.218(18)
C41a	-0.0110	0.3820	0.7830	0.096(25)
C42a	-0.0515(18)	0.3879(18)	0.8572(42)	0.071(15)
C43a	-0.0490	0.4410	0.9073	0.105(21)
C44a	-0.0968(37)	0.4494(29)	0.9623(70)	0.170(34)
C41b	-0.0221	0.3830	0.7830	0.057(12)
C42b	0.0038(13)	0.3898(13)	0.8773(28)	0.077(11)
C43b	-0.0063(15)	0.4426(15)	0.9272(34)	0.103(14)
C44b	-0.0612	0.4530	0.9679	0.156(22)

* S.o.f. 0.40 for C41a-C44a and 0.60 for C41b-C44b

Table 2. Selected distances (Å) and angles (°) in the mercury-sulfur network

Hg(1)-S(2)	2.482(5)	S(1)-Hg(1)-S(1 ⁱ)	94.3(2)
Hg(1)-S(3)	2.522(4)	S(1)-Hg(1)-S(2)	114.5(2)
Hg(1)-S(1)	2.549(5)	S(1)-Hg(1)-S(3)	106.4(2)
Hg(1)-S(1 ⁱ)	2.628(5)	S(1 ⁱ)-Hg(1)-S(2)	113.0(2)
		S(1 ⁱ)-Hg(1)-S(3)	102.4(2)
Hg(2)-S(4 ⁱⁱ)	2.500(5)	S(2)-Hg(1)-S(3)	122.2(1)
Hg(2)-S(4)	2.524(5)		
Hg(2)-S(3)	2.535(5)	S(2 ⁱⁱⁱ)-Hg(2)-S(3)	106.1(2)
Hg(2)-S(2 ⁱⁱⁱ)	2.584(4)	S(2 ⁱⁱⁱ)-Hg(2)-S(4)	115.0(1)
		S(2 ⁱⁱⁱ)-Hg(2)-S(4 ⁱⁱ)	103.7(2)
Hg(1)-Hg(1 ⁱ)	3.521(2) Å	S(3)-Hg(2)-S(4)	105.0(2)
Hg(2)-Hg(2) ≥	3.892(2) Å	S(3)-Hg(2)-S(4 ⁱⁱ)	117.9(2)
Hg(1)-Hg(2) ≥	3.965(1) Å	S(4)-Hg(2)-S(4 ⁱⁱ)	109.5(2)
Hg(1)-S(1)-Hg(1 ⁱ)	85.7(2)		
Hg(1)-S(2)-Hg(2 ^{iv})	103.0(2)		
Hg(1)-S(3)-Hg(2)	106.8(2)		
Hg(2)-S(4)-Hg(2 ⁱⁱⁱ)	101.5(2)		

Symmetry code: (i) $1/2-x, 1/2-y, 1/2-z$
(ii) $-1/4+y, 1/4-x, 1/4-z$
(iii) $1/4-y, 1/4+x, 1/4-z$
(iv) $x, 1/2-y, 1/4-z$

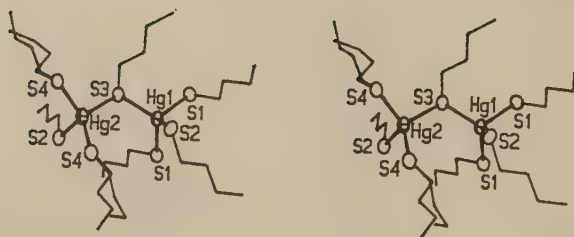


Fig. 1. The environment of the Hg atoms. Atomic numbering scheme is given in Table 2.

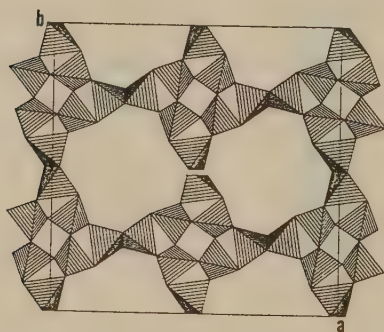


Fig. 2. Projection along c showing the Hg-S network of tetrahedra. Edgesharing occurs between $\text{Hg}(1)\text{S}_4$ groups. The tetrahedra in the middle are separated by one unit translation along c .



Structure of (Tetrahydroselenophene)mercury(II) Chloride

BY CLAES STÅLHANDSKE* AND FRANK ZINTL

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Abstract. $[\text{Hg}(\text{C}_4\text{H}_8\text{Se})]\text{Cl}_2$, $M_r = 406.6$, triclinic, $P1$, $a = 9.554(1)$, $b = 7.619(1)$, $c = 5.926(1)$ Å, $\alpha = 97.57(1)$, $\beta = 104.48(2)$, $\gamma = 89.72(1)^\circ$, $V = 413.8(1)$ Å³, $Z = 2$, $D_x = 3.26$ Mg m⁻³, $\lambda(\text{MoK}_\alpha) = 0.7107$ Å, $\mu = 24.2$ mm⁻¹, $F(000) = 360$, $T = 295$ K. $R = 0.042$ for 1747 observed reflections. Coordination around Hg is a distorted trigonal bipyramid with two short bonds Hg-Se 2.535(1), Hg-Cl 2.354(2) and three longer Hg-Cl 2.63-3.16 Å. The compound is isomorphous with $[\text{Hg}(\text{C}_4\text{H}_8\text{S})]\text{Cl}_2$.

*To whom correspondence should be addressed.

Experimental. Transparent needles crystallized from a methanol solution of tetrahydroselenophene and HgCl_2 . Crystal size $0.40 \times 0.07 \times 0.06$ mm. Enraf-Nonius CAD-4 diffractometer, graphite monochromatized MoK radiation, ω -2 θ scans. Cell dimensions from setting angles of 25 reflections $22^\circ < 2\theta < 36^\circ$. Data collected to $\sin\theta/\lambda = 0.47 \text{ \AA}$, h -12 to 12, k -9 to 9, l = -7 to 0, 2923 reflections collected, 2052 unique ($R_{\text{int}} = 0.03$), 1747 with $I > 3\sigma(I)$ used in the refinement, standard reflections $\bar{5}10$, $12\bar{3}$, $2\bar{4}\bar{2}$, 4 % random variation. L_p and absorption corrections, transmission factors 0.15-0.34. Structure refined with starting parameters from $\text{HgCl}_2 \cdot \text{C}_4\text{H}_8\text{S}$ (Bränden, 1964). Full-matrix least-squares techniques minimizing $\sum w\Delta F^2$; $w^{-1} = [\sigma^2(F_o) + (0.05 \cdot F_o)^2]$. Final refinements with H-atoms included in calculated positions with isotropic thermal parameters set to 1.2 times B_{eq} of the bonded atom. Model converged with 1747 reflections, 74 variables, $R = 0.042$, $wR = 0.054$, $(\Delta/\sigma)_{\text{max}} = 0.01$, $S = 0.99$, isotropic extinction parameter $0.59(4) \times 10^{-4}$, final Δ_{ρ} excursions $\leq 3.2 \text{ e \AA}^{-3}$. Scattering factors from International Tables for X-ray Crystallography (1974). Programs used: see Lundgren (1982).

Atomic coordinates and equivalent isotropic temperature factors are given in Table 1*. Selected bond distances, angles and torsion angles are presented in Table 2. The building elements of the structure, infinite double chains, are shown in Fig 1.

*List of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No SUP

Related literature. The crystal structure of $\text{HgCl}_2 \cdot \text{C}_4\text{H}_8\text{S}$ (Brändén, 1964),
 $\text{HgCl}_2 \cdot 2\text{C}_4\text{H}_8\text{S}$ and $\text{HgBr}_2 \cdot 2\text{C}_4\text{H}_8\text{S}$ (Sandström & Persson,
1986)

We thank Dipl chem Klaus Dreisch for synthesizing tetrahydroselenophene.

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Table 1. Coordinates and equivalent isotropic thermal parameters

	x	y	z	$B_{eq}^* (\text{\AA}^2)$
Hg	0.06393(3)	0.18614(4)	0.28375(5)	2.98(1)
Se	-0.1612(1)	0.3558(1)	0.3129(2)	3.02(2)
Cl(1)	0.0189(2)	0.1501(2)	0.7870(3)	3.31(5)
Cl(2)	0.3184(2)	0.1993(4)	0.3912(5)	4.32(7)
C(1)	-0.3142(11)	0.1695(14)	0.2036(19)	4.3(3)
C(2)	-0.4226(11)	0.2390(15)	0.0061(23)	4.8(3)
C(3)	-0.3391(11)	0.3241(14)	-0.1397(20)	4.7(3)
C(4)	-0.2288(10)	0.4524(12)	0.0100(20)	3.9(2)

$$*B_{eq} = 4/3(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\beta_{12}\cos\gamma + ac\beta_{13}\cos\beta + bc\beta_{23}\cos\alpha)$$

Table 2. Selected distances (Å), angles (°) and torsion angles (°)

Hg-Se	2.535(1)	Se-C(1)	1.969(10)
Hg-Cl(2)	2.353(2)	Se-C(4)	1.986(11)
Hg-Cl(1 ⁱ)	2.634(2)	C(1)-C(2)	1.508(16)
Hg-Cl(1 ⁱⁱ)	2.842(2)	C(2)-C(3)	1.516(16)
Hg-Cl(1)	3.165(2)	C(3)-C(4)	1.472(14)
Se-Hg-Cl(1 ⁱ)	104.94(5)	Hg ⁱ -Cl(1)-Hg ⁱⁱⁱ	94.97(6)
Se-Hg-Cl(1 ⁱⁱ)	97.94(5)	Hg ⁱ -Cl(1)-Hg	99.22(6)
Se-Hg-Cl(1)	74.02(5)	Hg-Cl(1)-Hg ⁱⁱⁱ	161.12(8)
Se-Hg-Cl(2)	144.37(7)	C(1)-Se-C(4)	89.6(4)
Cl(1 ⁱ)-Hg-Cl(1 ⁱⁱ)	85.03(6)	Se-C(1)-C(2)	104.7(7)
Cl(1 ⁱ)-Hg-Cl(1)	80.78(6)	C(1)-C(2)-C(3)	107.8(8)
Cl(1 ⁱⁱ)-Hg-Cl(1)	161.12(8)	C(2)-C(3)-C(4)	111.0(10)
Cl(1 ⁱ)-Hg-Cl(2)	107.63(9)	C(3)-C(4)-Se	105.7(7)
Cl(1 ⁱⁱ)-Hg-Cl(2)	98.87(9)		
Cl(1)-Hg-Cl(2)	97.25(8)		
Hg-Se-C(1)-C(2)	-125.4(7)		
Hg-Se-C(4)-C(3)	95.3(7)		
Se-C(1)-C(2)-C(3)	41.5(10)		
C(1)-C(2)-C(3)-C(4)	-51.5(12)		
C(2)-C(3)-C(4)-Se	33.4(10)		
C(3)-C(4)-Se-C(1)	-7.3(8)		
C(4)-Se-C(1)-C(2)	-19.3(8)		

Symmetry code: (i) -x,-y,l-z; (ii) x,y,z-l; (iii) x,y,z+1

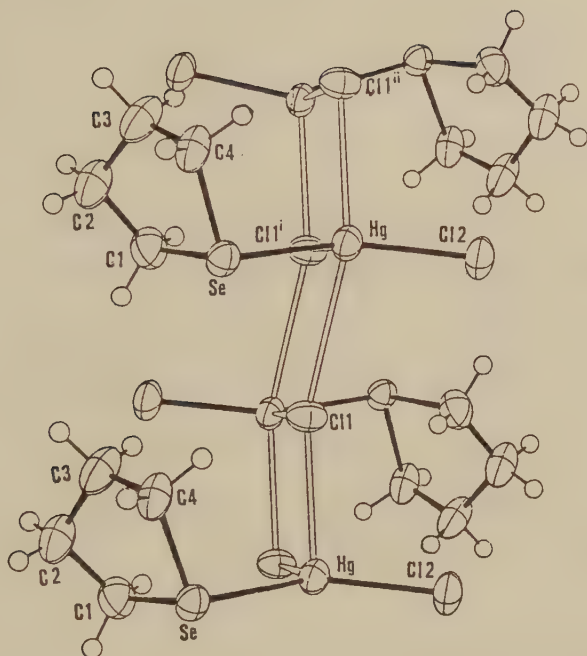


Fig 1. The infinite double chains in the structure and atomic numbering.

Anisotropic thermal parameters for non-hydrogen atoms. The form of the temperature factor is $\exp(-\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)$.

Atom	β_{11}	β_{22}	β_{32}	β_{12}	β_{13}	β_{23}
Hg	0.00702(5)	0.01407(8)	0.02435(15)	-0.00077(4)	0.00166(5)	0.00278(6)
Se	0.00827(10)	0.01333(15)	0.02183(27)	0.00050(9)	0.00174(13)	-0.00126(15)
Cl(1)	0.0133(3)	0.0121(3)	0.0206(6)	-0.0019(2)	0.0048(3)	0.0018(3)
Cl(2)	0.063(2)	0.0256(6)	0.0371(9)	-0.0017(3)	0.0013(4)	0.0075(6)
C(1)	0.010(1)	0.021(2)	0.039(4)	0.001(1)	0.006(2)	0.011(2)
C(2)	0.009(1)	0.022(2)	0.045(4)	-0.002(1)	-0.002(2)	0.007(2)
C(3)	0.010(1)	0.020(2)	0.040(4)	-0.004(1)	-0.005(2)	0.011(2)
C(4)	0.008(1)	0.015(2)	0.042(4)	-0.001(1)	0.000(2)	0.010(2)

Calculated hydrogen atom parameters

Atom	x	y	z	B
H(1C1)	-0.277	0.051	0.151	4.9
H(2C1)	-0.360	0.142	0.331	4.9
H(1C2)	-0.488	0.142	-0.095	5.4
H(2C2)	-0.483	0.331	0.070	5.4
H(1C3)	-0.291	0.227	0.778	4.9
H(2C3)	-0.409	0.385	0.743	4.9
H(1C4)	-0.268	0.573	0.034	4.6
H(2C4)	-0.146	0.467	-0.063	4.6

Structure of Dibromobis(tetrahydroselenophene)mercury(II) and
Diiodobis(tetrahydroselenophene)mercury(II)

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Abstract. $[\text{HgBr}_2(\text{SeC}_4\text{H}_8)_2]$, $M_r = 630.53$, monoclinic, Cc, $a = 23.551(3)$, $b = 5.1288(5)$, $c = 14.596(2)$ Å, $\beta = 128.14(1)^\circ$, $v = 1386.6(2)$ Å³, $z = 4$, $D_x = 3.02$ g cm⁻³, $\lambda(\text{MoK}_\alpha) = 0.71069$, $\mu = 220$ cm⁻¹, $F(000) = 1000$, $T = 295$ K, $R = 0.026$ for 1083 observed unique reflections. $[\text{HgI}_2(\text{SeC}_4\text{H}_8)_2]$, $M_r = 724.53$, triclinic, P1, $a = 5.1653(8)$, $b = 9.0009(12)$, $c = 16.884(4)$ Å, $\alpha = 92.21(2)$, $\beta = 91.29(2)$, $\gamma = 101.75(2)^\circ$, $v = 767.6(2)$ Å³, $z = 2$, $D_x = 3.13$ g cm⁻³, $\lambda(\text{MoK}_\alpha) = 0.71069$, $\mu = 187$ cm⁻¹, $F(000) = 572$, $T = 295$ K, $R = 0.039$ for 2122 observed unique reflections. Both compounds consist of monomeric species with the Hg atoms fourcoordinated by two halogen atoms and two tetrahydroselenophene ligands. The Hg coordination polyhedron is a distorted tetrahedron with (I)Br-Hg-Br(I) and Se-Hg-Se bond angles of 110.1° (119.3 , 122.4°) and 114.8° (107.6 , 111.9°). The Hg-Br(I) and Hg-Se distances are 2.60 , 2.61 Å (2.71 - 2.79 Å) and 2.62 , 2.67 Å (2.68 - 2.75 Å).

*To whom correspondence should be addressed.

Introduction. Compounds of mercury(II) halides with neutral organic sulfur, selenium or tellurium ligands show a remarkable variety in composition, structures and spectroscopic properties. The composition of thioether complexes ($L = RSR'$) can e.g. range from $(HgX_2)_2 \cdot L$ to $HgX_2 \cdot 2L$ with $3HgX_2 \cdot 2L$ and $HgX_2 \cdot L$ being the common forms between the extremes.

As has been confirmed by numerous crystallographic investigations, monomeric as well as halogene bridged dimeric and polymeric structures occur. Brändén (1964a,b) reported the crystal structures of $(HgCl_2)_2 \cdot SEt_2$ and $HgCl_2 \cdot THT$ ($THT = \text{tetrahydrothiophene}$), both consisting of polymeric chains built up by halogene bridges. $HgCl_2 \cdot THSe$ ($THSe = \text{tetrahydro-selenophene}$), isomorphous with $HgCl_2 \cdot THT$ has recently been refined (Stålhandske & Zintl, 1986). Sandström & Persson (1986) have investigated the structures of $HgX_2 \cdot 2THT$ ($X = Cl, Br$) in the solid state and, together with Goggin (1986), the bromide and iodide in THT solution. They found, both in the solid compounds and in the THT solutions, a distorted tetrahedral arrangement around Hg with two halogenes and two THT sulfur atoms.

Experimental. Summary of experiments and refinements are given in Table 1. Crystals were grown from a solution of mercury(II) bromide (iodide) in warm acetonitrile on addition of excess of THSe, followed by slow cooling to room temperature. Single crystals of the two compounds were sealed in Lindemann capillaries together with little mother liquid. Enraf-Nonius CAD-4 diffractometer, graphite monochromatized MoK_α radiation ω -2 θ scans. In the full-matrix least-squares refinements of $\text{HgBr}_2(\text{SeC}_4\text{H}_8)_2$ a parameter was included to correct for secondary extinction (Zachariasen, 1967). Scattering factors and anomalous dispersion factors from International Tables for X-ray Crystallography (1974). Refinements for $\text{HgI}_2(\text{SeC}_4\text{H}_8)_2$ gave unrealistic values for some distances and angles in the organic ligands and soft constraints were therefore included in the refinements, using SHELX76 (Sheldrick, 1976). Other programs used: see Lundgren (1982).

Discussion. Final atomic coordinates and temperature factors are listed in Table 2*, selected interatomic distances and angles are given in Table 3. The $\text{HgBr}_2(\text{SeC}_4\text{H}_8)_2$ molecule is drawn in Fig. 1 and Fig. 2 shows the molecular packing of the $\text{HgI}_2(\text{SeC}_4\text{H}_8)_2$ molecules in the unit cell.

The present compounds have as expected molecular structures with the Hg atoms coordinating two halogenes and two THSe selenium atoms forming distorted tetrahedra, as also found for the solid THT complexes (Sandström & Persson, 1986). The corresponding chloride complex has not yet been prepared either with THT or THSe, but the structures of $\text{HgCl}_2(\text{THT})$ (Brändén, 1964b) and $\text{HgCl}_2(\text{THSe})$ (Stålhandske & Zintl, 1986)

*List of structure factors, anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP...

have been solved. The two independent Hg tetrahedra in $\text{HgI}_2(\text{SeC}_4\text{H}_8)_2$ are slightly differently distorted (Table 3), probably due to packing effects.

In Table 4 distances and angles are given for tetrahedrally coordinated Hg atoms in $\text{HgX}_2 \cdot \text{L}_2$ compounds with $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and $\text{L} = \text{THT}, \text{THSe}$ or pyridine. The data show a clear tendency between bond lengths from Hg to L, X and the L-Hg-L and X-Hg-X angles. As expected, when the angle decreases the bond lengths will increase and vice versa. This is probably due to repulsion forces. Lower limits for the distances X-X, L-L and X-L seem to exist for the different ligand atoms and may be used as a measure of the effective radii for these atoms.

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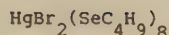
ZACHARIASEN, W.H. (1967). Acta Cryst. 23, 558-564.

Table 1. Summary of experiments and refinements

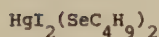
Compound	$\text{HgBr}_2(\text{SeC}_4\text{H}_8)_2$	$\text{HgI}_2(\text{SeC}_4\text{H}_8)_2$
Crystal dimensions (mm)	0.48 x 0.12 x 0.08	0.29 x 0.12 x 0.10
Number of reflections for lattice parameters and their 2θ range ($^\circ$)	50 20 < 2θ < 35	50 22 < 2θ < 40
Data collection ($2\theta_{\text{max}}$)	55	50
Scan width ($^\circ$)	0.70 + 0.5 $\tan\theta$	0.75 + 0.5 $\tan\theta$
Standard reflections (and % variation)	712, 425 934 (4 %)	318, 155 (5 %)
Number of measured reflections	1620	2878
Number of unique reflections	1365	2458
R_{int}	0.038	0.035
Reflections with $I > 3\sigma(I)$	1083	2122
Least-squares parameters	77	157
Transmission factor range	0.09 - 0.36	0.13 - 0.25
Weights (w^{-1})	$\sigma^2(F_o) + (0.018 \cdot F_o)^2 + 2.0$	$\sigma^2(F_o) + (0.06 \cdot F_o)^2$
Largest Δ/σ in final cycle	0.08	0.35
$\Delta\rho_{\text{max}}$ ($\text{e } \text{\AA}^{-3}$)	0.84	1.63
$R(F)$	0.026	0.039
$\omega R(F)$	0.032	0.040
Secondary extinction parameter, g	$0.21(3) \cdot 10^{-4}$	-

Table 2. Atomic coordinates and isotropic temperature factors $\text{\AA}^2$

$$U_{eq} = \frac{1}{3} \sum_i U_{ii} a_i^* a_i^* a_i a_i$$



Atom	x/a	y/b	z/c	Uiso/Ueq
Hg	0.0000	0.1297(1)	0.2500	0.0420(3)
Br1	0.0883(3)	0.4189(9)	0.2429(5)	0.0492(25)
Br2	-0.0872(3)	0.4221(9)	0.2570(5)	0.0514(26)
Se1	-0.0806(3)	-0.1533(8)	0.0549(4)	0.0379(20)
Se2	0.0787(3)	-0.1433(8)	0.4426(5)	0.0444(24)
C1	-0.1804(9)	-0.0533(34)	-0.0050(16)	0.032(4)
C2	-0.1981(14)	0.1938(51)	-0.0539(20)	0.046(6)
C3	-0.1693(10)	0.1940(37)	-0.1305(15)	0.033(4)
C4	-0.0887(14)	0.1406(43)	-0.0489(21)	0.047(6)
C5	0.1732(13)	-0.0720(44)	0.4853(20)	0.052(7)
C6	0.1962(14)	0.1886(52)	0.5761(21)	0.048(6)
C7	0.1718(14)	0.1237(50)	0.6520(21)	0.062(7)
C8	0.0907(13)	0.0842(41)	0.5628(19)	0.035(5)



Atom	x/a	y/b	z/c	Uiso/Ueq
Hg1	0.0000	0.0000	0.0000	0.0430(4)
Hg2	0.3251(2)	0.0745(1)	0.5270(1)	0.0461(5)
I1	-0.2210(5)	0.1773(3)	0.1081(1)	0.0505(8)
I2	-0.3251(6)	-0.1903(3)	-0.1079(2)	0.0574(8)
I3	0.6406(5)	0.2633(3)	0.6351(2)	0.0589(8)
I4	0.5195(5)	-0.1039(3)	0.4193(2)	0.0579(9)
Se1	0.3580(7)	0.1819(4)	-0.0840(3)	0.0540(13)
Se2	0.2231(8)	-0.1866(5)	0.0875(3)	0.0567(13)
Se3	0.0738(7)	0.2621(5)	0.4430(2)	0.0449(10)
Se4	-0.0443(6)	-0.1080(4)	0.6095(2)	0.0469(11)
C1	0.3098(64)	0.3770(25)	-0.0303(15)	0.078(7)
C2	0.1153(68)	0.4330(34)	-0.0844(17)	0.069(6)
C3	0.1633(60)	0.3868(26)	-0.1713(14)	0.065(5)
C4	0.1092(34)	0.2163(18)	-0.1731(9)	0.033(4)
C5	0.1611(39)	-0.1150(20)	0.1954(9)	0.036(6)
C6	0.0071(53)	-0.2626(30)	0.2311(13)	0.079(6)
C7	-0.1949(50)	-0.3595(28)	0.1696(14)	0.069(8)
C8	-0.1052(46)	-0.3538(26)	0.0910(15)	0.071(5)
C9	0.1003(52)	0.2031(31)	0.3279(11)	0.074(8)
C10	0.3943(40)	0.2795(22)	0.3091(12)	0.054(5)
C11	0.4309(62)	0.4410(29)	0.3417(16)	0.084(7)
C12	0.3607(46)	0.4406(23)	0.4318(14)	0.059(8)
C13	-0.0311(37)	-0.3107(17)	0.5681(11)	0.032(7)
C14	0.2009(50)	-0.3526(27)	0.6139(14)	0.045(11)
C15	0.2037(54)	-0.2984(26)	0.6989(14)	0.062(6)
C16	0.1339(73)	-0.1320(35)	0.7119(14)	0.098(6)

Table 3. Selected bond lengths (Å) and angles (°)

In $\text{HgBr}_2(\text{SeC}_4\text{H}_8)_2$

Hg-Br(2)	2.596(6)	Br(1)-Hg-Br(2)	110.1(2)
Hg-Br(1)	2.609(6)	Se(1)-Hg-Se(2)	114.8(2)
Hg-Se(2)	2.620(5)	Br(1)-Hg-Se(1)	109.0(2)
Hg-Se(1)	2.672(5)	Br(1)-Hg-Se(2)	107.1(2)
		Br(2)-Hg-Se(1)	107.3(2)
		Br(2)-Hg-Se(2)	108.6(2)
Se(1)-C(1)	2.00(2)	C(1)-Se(1)-C(4)	86.6(9)
Se(1)-C(4)	2.06(2)	Se(1)-C(1)-C(2)	111.0(15)
C(1)-C(2)	1.39(3)	C(1)-C(2)-C(3)	103.5(19)
C(2)-C(3)	1.63(3)	C(2)-C(3)-C(4)	108.1(16)
C(3)-C(4)	1.52(3)	C(3)-C(4)-Se(1)	102.2(15)
Se(2)-C(5)	1.94(2)	C(5)-Se(2)-C(8)	95.5(10)
Se(2)-C(8)	1.98(2)	Se(2)-C(5)-C(6)	98.5(14)
C(5)-C(6)	1.71(3)	C(5)-C(6)-C(7)	107.5(19)
C(6)-C(7)	1.57(3)	C(6)-C(7)-C(8)	103.8(19)
C(7)-C(8)	1.52(3)	C(7)-C(8)-Se(2)	104.8(15)

In $\text{HgI}_2(\text{SeC}_4\text{H}_8)_2$

Hg(1)-Se(1)	2.680(4)	I(1)-Hg(1)-I(2)	119.3(1)
Hg(1)-Se(2)	2.688(4)	Se(1)-Hg(1)-Se(2)	111.9(1)
Hg(1)-I(2)	2.741(3)	I(1)-Hg(1)-Se(1)	109.2(1)
Hg(1)-I(1)	2.786(2)	I(1)-Hg(1)-Se(2)	105.9(1)
		I(2)-Hg(1)-Se(1)	106.2(1)
		I(2)-Hg(1)-Se(2)	104.2(1)

Table 3. continued.

Se(1)-C(1)	2.00(3)	C(1)-Se(1)-C(4)	86.8(10)
Se(1)-C(4)	2.03(2)	Se(1)-C(1)-C(2)	106.0(19)
C(1)-C(1)	1.51(4)	C(1)-C(2)-C(3)	105.5(24)
C(2)-C(3)	1.53(4)	C(2)-C(3)-C(4)	104.4(19)
C(3)-C(4)	1.49(3)	C(3)-C(4)-Se(1)	101.5(4)
Se(2)-C(5)	1.96(2)	C(5)-Se(2)-C(8)	89.7(9)
Se(2)-C(8)	2.01(2)	Se(2)-C(5)-C(6)	102.1(12)
C(5)-C(6)	1.55(3)	C(5)-C(6)-C(7)	111.2(18)
C(6)-C(7)	1.56(4)	C(6)-C(7)-C(8)	111.3(21)
C(7)-C(8)	1.39(4)	C(7)-C(8)-Se(2)	110.4(17)
Hg(2)-Se(4)	2.701(3)	I(3)-Hg(2)-I(4)	122.4(1)
Hg(2)-I(3)	2.718(3)	Se(3)-Hg(2)-Se(4)	107.6(1)
Hg(2)-I(4)	2.728(3)	I(3)-Hg(2)-Se(3)	104.7(1)
Hg(2)-Se(3)	2.748(4)	I(3)-Hg(2)-Se(4)	106.8(1)
		I(4)-Hg(2)-Se(3)	106.9(1)
		I(4)-Hg(2)-Se(4)	107.6(1)
Se(3)-C(9)	1.99(2)	C(9)-Se(3)-C(12)	90.3(11)
Se(3)-C(12)	1.94(2)	Se(3)-C(9)-C(10)	104.7(14)
C(9)-C(10)	1.57(3)	C(9)-C(10)-C(11)	104.0(18)
C(10)-C(11)	1.52(3)	C(10)-C(11)-C(12)	110.0(18)
C(11)-C(12)	1.59(4)	C(11)-C(12)-Se(3)	105.8(16)
Se(4)-C(13)	1.94(2)	C(13)-Se(4)-C(16)	95.3(10)
Se(4)-C(16)	1.96(2)	Se(4)-C(13)-C(14)	104.5(13)
C(13)-C(14)	1.52(3)	C(13)-C(14)-C(15)	110.7(20)
C(14)-C(15)	1.49(3)	C(14)-C(15)-C(16)	115.2(19)
C(15)-C(16)	1.62(4)	C(15)-C(16)-Se(4)	101.2(15)

Table 4. A comparison of the bond lengths $d(\text{Hg-X})$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $d(\text{Hg-L})$, ($\text{L} = \text{pyridine}, \text{THT}, \text{THSe}$) with the bond angles $\angle \text{X-Hg-X}$ and $\angle \text{L-Hg-L}$ in pseudotetrahedral L_2HgX_2 complexes. Mean values are given for the distances in the solids.

Compound	$\bar{d}(\text{Hg-X})$ in Å	$\bar{d}(\text{H-L})$ in Å	$\angle(\text{X-Hg-X})$	$\angle(\text{L-Hg-L})$
HgCl_2 in pyridine ^a	2.375	2.47	150	
$\text{HgCl}_2(\text{THT})_2$ ^b	2.439	2.58	115.1	109.1
HgBr_2 in pyridine ^a	2.497	2.45	147	
$\text{HgBr}_2(\text{py})_2$ ^c	2.481	2.39	141.2	90.7
HgBr_2 in ^d THT	2.535	2.62	130	
$\text{HgBr}_2(\text{THT})_2$ ^b	2.553	2.60	117.5	107.7
$\text{HgBr}_2(\text{THSe})_2$ ^e	2.603	2.65	110.1	114.8
HgI_2 in pyridine ^a	2.665	2.43	141	
$\text{HgI}_2(\text{py})_2$ ^a	2.666	2.424	142.7	93.8
HgI_2 in THT ^d	2.670	2.72	143	
$\text{HgI}_2(\text{THSe})_2$ ^e	2.764	2.68	119.3	111.9
	2.723	2.72	122.4	107.6

^aPersson, Sandström, Goggin, Mosset (1985).

^bSandström, Persson (1986).

^cCanty, Raston, Skelton, White (1982).

^dSandström, Persson, Goggin (1986).

^ePresent work.

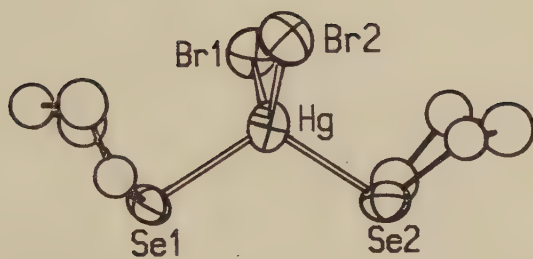


Fig 1. The $\text{HgBr}_2(\text{SeC}_4\text{H}_8)_2$ molecule

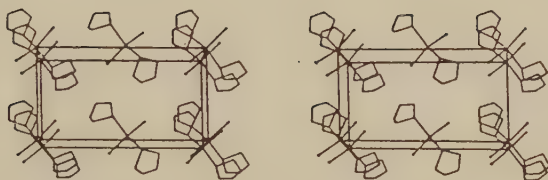


Fig 2. Stereoview of the molecular packing in $\text{HgI}_2(\text{SeC}_4\text{H}_8)_2$

V

Interactions of d¹⁰ Metal Ions and Organic Sulfur Ligands in Non-Aqueous Solvents. A Thermodynamic Study on the Complex Formation Between Mercury(II) and Thiolates in Pyridine, and Between Silver(I) and Various Sulfides in Pyridine and Dimethylsulfoxide.

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ABSTRACT

The complex formation between mercury(II) and selected sodium thiolates and corresponding thiols in dilute pyridine solution, and between silver(I) and selected organic sulfides in dilute pyridine and DMSO solutions, was investigated by electrochemical and calorimetric measurements. The stability constants and heats for the stepwise complex formation were determined, and the complex formation entropies were calculated from these. The results are in close agreement with the tendencies which have been found for the coordination behaviour of organic chalcogene ligands towards mercury(II) and silver(I) in other solvent systems, and the solid state.

INTRODUCTION

Organic compounds containing sulfur atoms with lone electron pairs have for a long time been known to form very stable complexes with the soft type d^{10} closed shell electron acceptors mercury(II), copper(I), silver(I) and gold(I). Compounds such as $Hg(SR)_2$, $Hg(SR)X$, $HgX_2 \cdot zSR_2$ and $MX \cdot zSR_2$, $M = Cu, Ag, Au$, $X = Cl, Br, I, O_2CR$, ClO_4 or BF_4 ; $z = 1-4$; $R =$ alkyl or aryl group, have been extensively studied by means of preparation[1-8], spectroscopy[7-17] and crystallography[5-19].

These studies have shown that the coordination to the metal ion normally is linear, trigonal or tetrahedral when large and soft donors, like sulfur, coordinate to the mercury(II) or silver(I) atom. Since the metal sulfur bonds are very strong in thiolate complexes of the monovalent acceptors copper(I), silver(I) and gold(I) and of mercury(II), the solid neutral compounds $MSR(M=Cu, Ag, Au)$ and $Hg(SR)$ are often polymers linked via $M-S(R)-M$ bridges and, consequently, many of them are virtually insoluble in aqueous media and often poorly soluble in weakly donating organic solvents, e.g. alcohols and ketones. Similar, but to a lower extent, is the case of the stability of the bond to be formed and the solubility of addition compounds between organic sulfides RSR' and the above mentioned metal acceptors.

The stepwise complex formation of silver(I) and organic sulfides has been extensively studied in aqueous solutions and water/alcohol mixtures[23-30]. In most of these systems, the consecutive formation of 2-4 complexes has been reported, suggesting that the coordination geometries around the central metal ion is linear, trigonal-planar, or tetrahedral. On the other hand, only few complex formation studies have been performed with mercury(II) and the same type of ligands and solvents[20-28]. This is mainly because that metal sulfide complexes, if the sulfide is not substituted with polar groups, have

low solubility in aqueous solution. In most of the previous investigations, the solubility of the sulfides and of their heavy metal complexes was increased by introduction of one or several polar groups, such as $-\text{OH}$, $-\text{SO}_3^-$, $-\text{CO}_2\text{H}$, or $-\text{NH}_3^+$, to the carbon chains bonded to sulfur[23-29]. The silver thiolates AgSR exhibit poor solubility even in solvents that are relatively strong donors to mercury(II) and silver(I), e.g. amines and pyridines. On the other hand, the mercuric thiolates $\text{Hg}(\text{SR})_2$ and the silver(I) and mercury(II) complexes with organic sulfides show sufficient solubility in these solvents to allow the investigation of complex formation even without introduction of any potentially competing polar groups on the ligands.

The purpose of this work was to examine the stepwise complex formation between some selected organic sulfides and silver(I) and mercury(II) in pyridine and DMSO solution, and the complex formation between two selected sodium thiolates and corresponding thiols and mercury(II) in pyridine, by electrochemical and calorimetical measurements. Ligands such as di-n-butylsulfide, diphenylsulfide, tetrahydrothiophene, 1-butanethiol, thiophenol, and the sodium salts of the latter two, were chosen.

EXPERIMENTAL

Chemicals. $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ and $\text{Hg}(\text{Py})_2(\text{ClO}_2)_2$ were used as mercury(II) sources and were prepared and analyzed as described elsewhere [31-33]. Anhydrous silver(I) perchlorate was used as source for silver(I). All sulfides and thiols were purified by distillation and stored under dry nitrogen in dark vessels. The distillations of diphenylsulfide and thiophenole were performed in vacuo, the other ligands were distilled in a stream of dry nitrogen at atmospheric pressure. Sodium thiophenolate was prepared from thiophenol and

sodium hydroxide in ethanol. Sodium thio-n-butylate was prepared in absolute alcohol from 1-butanethiol and metallic sodium under nitrogen. The white solid products were obtained by boiling off the ethanol under nitrogen atmosphere. The sodium thiolates, and all pyridine solutions prepared from them, were analyzed according to previously described methods[34]. Whereby the analysis of solutions were repeated twice a day during storage (see below). DMSO was purified and stored as described previously[35]. Pyridine was purified by refluxing over potassium hydroxide for two hours, followed by distillation over potassium hydroxide.

Reactions with thiols and thioplates. Stock pyridine solutions containing thiols and thiolate decompose, probably from air oxidation. Disulfides or sulfonates are most probably formed at oxidation. The decomposition reactions are, however, slow enough to allow electrochemical and calorimetric measurements as they were performed in this work.

Choice of media. 1.0 M ammonium perchlorate and 0.1 M tetraethylammonium perchlorate were used as supporting electrolyte in DMSO and pyridine, respectively.

Potentiometric measurements. Metallic mercury reduces the solvated mercury(II) ion according to $\text{Hg(l)} + \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+}$. The reproporation constant

$K_R = [\text{Hg}_2^{2+}][\text{Hg}^{2+}]^{-1}$ has previously been determined to 24.0(2.0) in DMSO with 1.0 M NH_4ClO_4 as the ionic medium[36] and to 0.171(0.005) in pyridine with 0.1 M Et_4NClO_4 as the ionic medium[33]. The mercury/mercury(II) electrode can therefore only be used in presence of ligands stabilizing mercury(II) over mercury(I). Fortunately this is the case for the studied thiolate ligands; no appreci-

able reproporationation was found in pyridine for the thiol and thiolate systems for $\bar{n} > 1.5$.

This implies that the stepwise constants K_j can be determined accurately by potentiometric measurements. To ensure that no solutions containing mercury(I) were included, the mercury electrode compartment initially contained solutions of mercury(II) perchlorate and the studied ligand in a C_L/C_M ratio between 4 and 6 for thiol and thiolates, and in a C_L/C_M ratio of about 50 for the thioethers. To these solutions, aliquots of a mercury(II) perchlorate solution of the same concentration as in the electrode vessel, were added. The mercury(II) concentration was thus constant during the titrations. Titrations with $C_M = 5, 10$ and 20 mM have been performed, while the ligand concentration ranged from 13 to 66 mM. A silver electrode, with a silver(I) concentration of 10 mM, was used as reference electrode.

In the silver(I) systems, silver(I) perchlorate solutions with an initial concentration, C_M , ranging between 3 - 20 mM, were directly titrated with thioether solutions with a ligand concentration C_L between 50 and 600 mM. Silver plates were used as electrodes and the reference cell contained a from the beginning a silver solution of the same composition as in the reaction vessel.

To exclude moisture and to decrease the oxygen concentration, all titrations were performed in a glove box. In addition, dried nitrogen, which had passed through a couple of flasks containing the ionic medium used, was bubbled through the electrode solutions throughout the titrations.

Calorimetric measurements. The calorimeter and the procedure used have been described previously[37].

The initial solutions, of 40-80 ml volume, had mercury(II) concentrations ranging from 3.0 to 16.0 mM. To these solutions, aliquots of ligand solution were added, totally 20 ml in each titration series. If the complex formation was not completed 20 ml were then withdrawn from the calorimeter vessel and the titration was continued. This procedure was repeated until the complex formation was complete. Heats of dilution were determined for the mercury(II) ion and for the ligands. The heats of dilution of the ligands were especially important because of the feared air oxidation of thiols and thiolates in pyridine.

Following the same routine, calorimetric titrations on the complex formation reactions of silver(I) -THT system in DMSO were performed.

Calculations. The emfs measured during the potentiometric titrations were used for calculation of the complex stability constants β_j by a computer program. Two different versions of this program were necessary. The version EMK[38] was applied for data of silver(I) systems where all the emfs needed to be corrected for dilution of the metal in solution according to Nernst's law. In the case of the mercury(I) systems no such dilution took place during the measurement. Here the version EMKBAK[38], without this correction, was used. The obtained calorimetric data were corrected for heats of dilution and from these the enthalpy changes have been calculated by the computer program KALORI[39]. The stability constants β_j obtained from the potentiometric measurements were introduced as fixed parameters in the calculations of the enthalpy changes.

WARNING: Great caution must be exercised when handling DMSO solutions containing mercury salts because of the skin-penetrating properties of DMSO [40,41]. Moreover, the ligands and ligand solutions must be kept under nitrogen in closed vessels not only because of their sensitivity to moisture and oxygen, but also because of their smell.

RESULTS

For silver(I), no complex formation could be proved to take place with di-n-butylsulfide in DMSO or pyridine, nor with diphenylsulfide in pyridine. The formation of one weak mononuclear complex was found with diphenylsulfide in DMSO, and with THT in pyridine. Only one system, $\text{Ag}^+ - \text{THT}$ in DMSO, shows the formation of two weak mononuclear complexes, $\text{Ag}(\text{THT})^+$ and $\text{Ag}(\text{THT})_2^+$. The complex formation constants β_j and the three energy changes ΔG_j° are given in Table I. In the case of the system $\text{Ag}^+ - \text{THT}$ in DMSO, the determination of ΔH_j° from calorimetric measurements allowed the calculation of the complex formation entropies ΔS_j° , $j=1,2$, all included in the same Table. The complex formation functions of the silver(I) and THT in pyridine coincides practically with that of silver(I) and diphenylsulfide in DMSO, and is therefore not shown. The complex distribution function for the system $\text{Ag}^+ - \text{THT}$ in DMSO is given in Fig. 2.

in DMSO, and is therefore not shown here. The complex distribution Furthermore, no complex formation between mercury(II) and thioethers has been found neither in DMSO nor in pyridine by the potentiometric calorimetric techniques used here. The stability constant of the first complex must be 10^4 M^{-1} or higher in order to determine stability constants of mercury(II) systems in DMSO with potentiometric technique described above. It is necessary to stabilize mercury(II) that it not reacts with metallic mercury forming disturbing amounts of mercury(I). Large enthalpy changes are necessary if stability constants shall be determined by calorimetric techniques. Mercury(II)

forms three strong complexes with thiolates in pyridine. In pyridine solution, the thiols will lose the proton bonded to sulfur to pyridine forming a pyridinium ion upon complex formation with mercury(II). The same complexes are thus formed independently of whether thiol or thiolate is used as the ligand.

The overall stability constants, β_j , calculated from the potentiometric data in pyridine are summarized in Table II. The complex formation and complex distribution functions of the mercury(II) complexes formed with the sodium thiolates are given in Fig. 3 and 4, respectively. The analogous functions for the complex formation between mercury(II) and the free thiols practically coincides with these.

The overall enthalpy changes, $\Delta H_{\beta_j}^{\circ}$, calculated from calorimetric data in pyridine are summarized in Table III. From the obtained β_j values, the stepwise stability constants K_j and the standard free energy changes ΔG_j° are calculated for each consecutive step. The stepwise enthalpy changes ΔH_j are calculated from the overall enthalpy changes $\Delta H_{\beta_j}^{\circ}$. The stepwise entropy changes ΔS_j° are obtained by combining the ΔG_j° and ΔH_j° values. The thermodynamic functions for the stepwise formation of mercury(II) thiol and thiolate complexes in pyridine are summarized in Table IV.

DISCUSSION

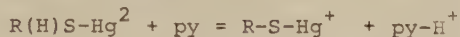
No complex formation has been proved in DMSO or pyridine between mercury(II) and thioethers; tetrahydrothiophene, diphenylsulfide and di-n-butylsulfide. In aqueous and alcoholic solutions [21-28], on the other hand two or more fairly strong mercury(II) thioether complexes are formed; these thioethers have polar groups necessary for sufficiently solubility in these solvents.

Studies of the donor properties of a large number of solvents to mercury(II) halides have shown that the thioethers are only slightly stronger donors than DMSO and pyridine, while water is a markedly weaker donor than the thioethers[42,43]. It is therefore reasonable that the larger activity of the solvent compensates for the somewhat stronger donor properties of the thioethers in DMSO and pyridine, and no complex formation takes place. In aqueous solution the water activity can not compensate for the large difference in donor strength, and consequently mercury(II) thioether complexes are formed.

The silver systems behaves similarly. The stronger donor solvent pyridine manages to suppress complex formation between silver(I) and two of the sulfides, while more weakly donating DMSO brings about this effect only for one of them. All three ligands, however, are known to form insoluble addition compounds when they are added to concentrated silver(I) solutions in water or water-alcohol mixtures [44].

Three very strong mercury(II) thiolate complexes are formed in pyridine. There are no indications of a fourth complex in any of the studied systems. The complex distribution follows an unusual pattern for mercury(II) complexes, where the second complex normally is strongly predominating. In these systems the first complex is very strongly predominating, while the second complex is suppressed. In pyridine, the second complexes never exceed 45% predominance, see Fig. 2. and the K_2/K_3 ratios in Table IV. The extraordinary stability of the mercury(II) thiolate complexes is shown by the formation of the final third complex, which is completed already at free ligand concentrations lower than 10 μ M. No mercury(II) thiol complex

are formed in pyridine due to the fairly strong basicity of pyridine. This means that the following equilibrium is established far to the right:



It is surprising that the mercury(II) thiophenolate complexes are stronger than the corresponding thiobutylate complexes. One possible explanation might be that the thiobutylate ion is a bulkier ligand than the thiophenolate ion. If the coordinated ligands tend to collide, the complex will be thermodynamically destabilized.

The very strong complex formation between mercury(II) and thiolates is characterized by very negative enthalpy changes, see Table III. The enthalpy changes are indeed for all steps so negative that the step-wise entropy changes are slightly negative with, a few exceptions. The very negative enthalpy changes indicate that very strong Hg-S bonds, with a high degree of covalency, are established at the formation of all mercury(II) thiolate complexes.

Structure determinations of the $Hg(S^nBu)_3^-$ and $Hg(SPh)_3^-$ in pyridine solution have shown that mercury(II) is trigonally coordinating the three thiolate ligands[45]. The mercury(II) pyridine solvate is six-coordinated in solution[46]. This means that one or several coordination switches take place during the consecutive complex formation.

ACKNOWLEDGEMENTS

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Table I. Overall stability (β_j/M^{-j}) and stepwise changes in free energy ($\Delta G_j/kJmol^{-1}$) of the silver(I) tetrahydrothiophene system in pyridine and DMSO and the silver(I) diphenylsulfide system in DMSO, and thermodynamic functions ($\Delta H_j^O/kJmol^{-1}$, $\Delta S_j^O/Jmol^{-1}K$) of silver(I) tetrahydrothiophene system in DMSO at 25°C. Medium 0.1 M Et_4NClO_4 in pyridine and 1.0 M NH_4ClO_4 in DMSO. The limits of error refer to three standard deviations.

Ligand	Pyridine, 0.1 M Et_4NClO_4		DMSO, 0.1 M NH_4ClO_4	
	THT	THT	THT	Ph_2S
β_1	0.89±0.04	17.5±2.6	536±30	3.0±0.2
β_2				
$-\Delta G_1^O$	-0.43	7.09	8.49	2.72
$-\Delta G_2^O$				
ΔH_1^O		-44.40		
ΔH_2^O				
ΔS_1^O		-125		
ΔS_2^O				
$-\Delta G_{\beta 2}^O$		15.58		
$-\Delta H_{\beta 2}^O$				
$\Delta S_{\beta 2}^O$				

Table II. Overall stability constants (β_j/M^{-j}) of mercury(II) thiol and thiolate complexes in pyridine at 25°C. Medium 0.1 M Et₄NClO₄. The limits of error refer to three standard deviations. NP denotes the number of observations for each system.

Ligand	PhS ⁻	PhSH	BuS ⁻	BuSH
β_1	(5.28±0.46) · 10 ¹⁰	(2.63±0.28) · 10 ¹⁰	(5.98±0.65) · 10 ⁹	(4.89±0.34) · 10 ⁹
β_2	(4.79±0.99) · 10 ¹⁹	(1.93±0.40) · 10 ¹⁸	(5.18±1.51) · 10 ¹⁶	(2.94±0.78) · 10 ¹⁶
β_3	(3.43±0.55) · 10 ²⁸	(7.66±1.62) · 10 ²⁵	(2.04±0.57) · 10 ²³	(1.75±0.31) · 10 ²³
NP	185	94	96	88

Table III. Overall enthalpy changes ($\Delta H_{\beta j}^{\circ}/\text{kJmol}^{-1}$) for the formation of mercury(II) thiol and thiolate complexes in pyridine at 25°C. Medium 0.1 M Et_4NClO_4 . The limits of error refer to three standard deviations; NP denotes the number of aliquots added for each system.

Ligand	PhS ⁻	PhSH	BuS ⁻	BuSH
$-\Delta H_{\beta 1}^{\circ}$	60.8±1.1	65.4±0.9	73.1±4.5	65.2±2.4
$-\Delta H_{\beta 2}^{\circ}$	115.1±2.4	124.7±1.8	112.3±11.9	97.5±5.6
$-\Delta H_{\beta 3}^{\circ}$	163.6±1.9	178.2±1.6	177.9±8.5	149.8±4.2
NP	22	54	51	76

Table IV. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions ΔG_j° , $\Delta H_j^{\circ}/kJmol^{-1}$; $\Delta S_j^{\circ}/Jmol^{-1}$) for the stepwise formation of mercury(II) thiolate and thiol complexes in pyridine at 25°C. Medium 0.1 M Et_4NClO_4 .

Ligand	PhS ⁻	PhSH	BuS ⁻	BuSH
log K_1	10.72	10.42	9.77	9.69
log K_2	8.96	7.87	6.94	6.78
log K_3	8.86	7.60	6.60	6.77
K_1/K_2	58.1	357	691	813
K_2/K_3	1.3	1.9	2.2	1.0
$-\Delta G_1^{\circ}$	61.2	59.5	55.8	55.3
$-\Delta G_2^{\circ}$	51.1	44.9	39.6	38.7
$-\Delta G_3^{\circ}$	50.5	43.4	37.7	38.7
$-\Delta H_1^{\circ}$	60.8	65.4	73.1	65.2
$-\Delta H_2^{\circ}$	54.4	59.3	39.2	32.3
$-\Delta H_3^{\circ}$	48.5	53.5	65.6	52.3
ΔS_1°	+2	-20	-58	-33
ΔS_2°	-11	-48	+1	+21
ΔS_3°	+7	-37	-94	-46
$-\Delta G_{\beta 3}^{\circ}$	162.9	147.7	133.0	132.7
$-\Delta H_{\beta 3}^{\circ}$	163.6	178.2	177.9	149.8
$\Delta S_{\beta 3}^{\circ}$	-2	-102	-151	-57

LEGENDS TO THE FIGURES

Fig. 1. Complex formation curves of the silver(I) tetrahydrothiophene(THT) and diphenylsulfide (Ph_2S) system.

Fig. 2. Distribution of silver(I) tetrahydrothiophene and diphenylsulfide (Ph_2S) complexes in DMSO.

Fig. 3. Complex formation curves of the mercury(II) 1-buthanethiolate and thiophenolate systems in pyridine.

Fig. 4. Distribution of mercury(II) 1-buthanethiolate and thiophenolate complexes in pyridine.

Fig. 1.

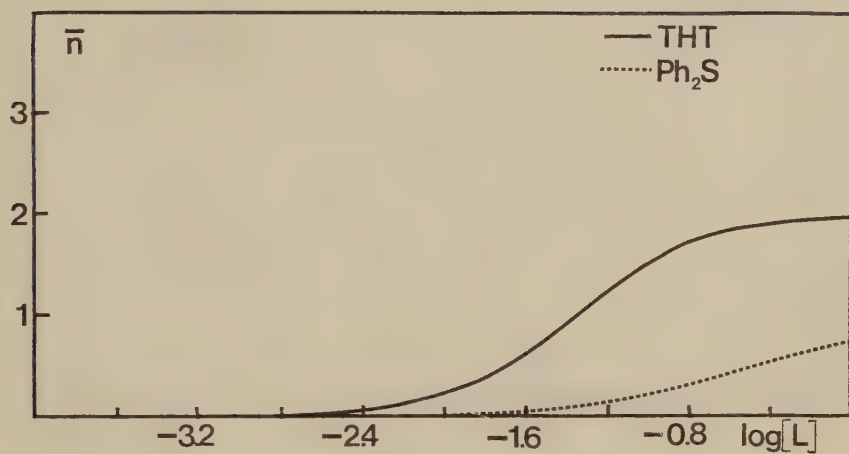


Fig. 2.

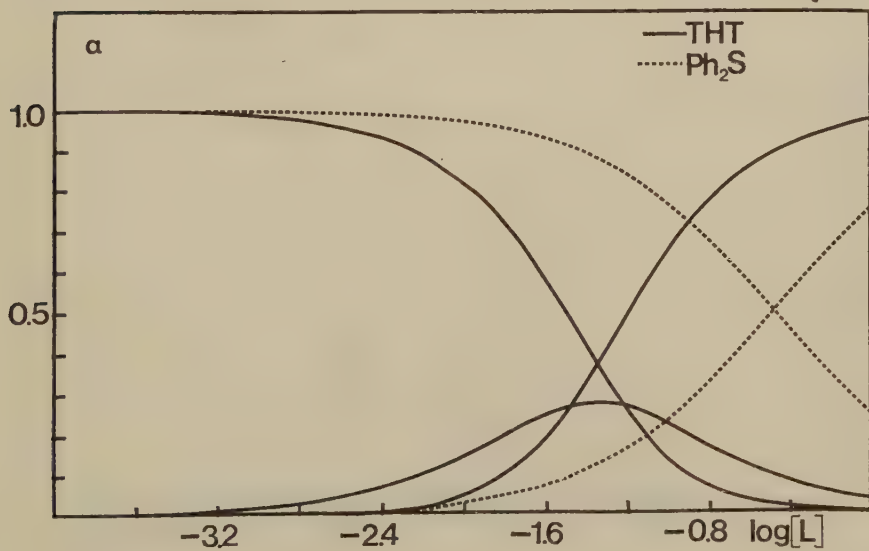


Fig. 3.

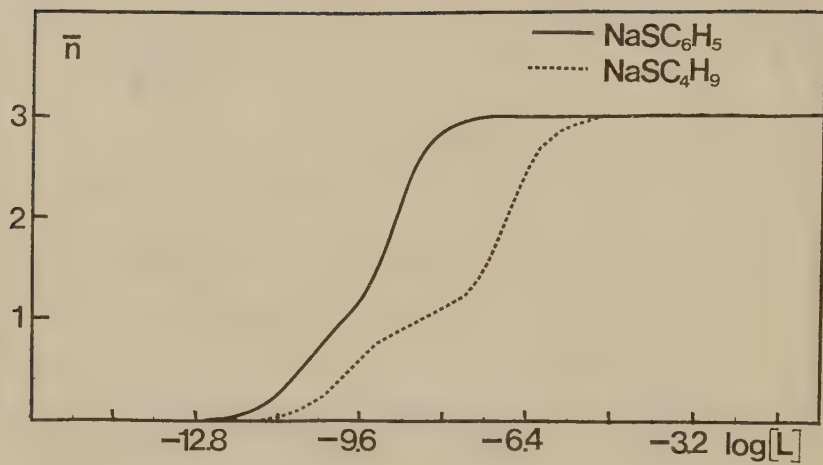
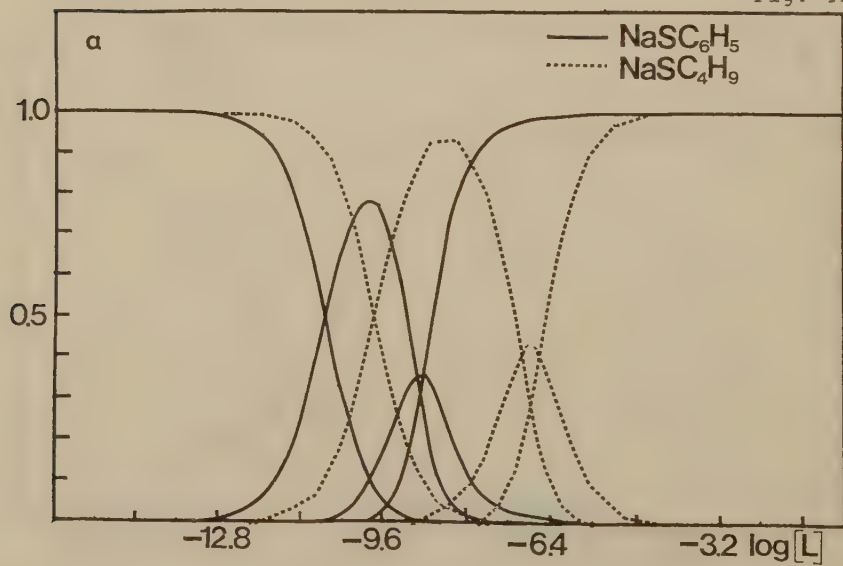


Fig. 4.



VI

A Structural Study of 1-Butanethiolatomercury(II)
Perchlorate, Pyridinium Tris(1-butanethiolato)mercu-
rate(II) and Pyridinium Tris(thiophenolato)mercurate(II)
in Pyridine Solution.

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ABSTRACT

The stereochemistry around mercury(II) in the $\text{Hg}(\text{SR})_3^-$, $\text{R} = {}^n\text{C}_4\text{H}_9$ and C_6H_5 , and $\text{Hg}_2(\text{SC}_4\text{H}_9)_2^{2+}$ complexes in pyridine solution has been studied by means of large angle X-ray scattering (LAXS) technique. The $\text{Hg}(\text{SR})_3^-$ complexes were found to be trigonal planar with mercury in the center of gravity and the sulfurs in the corners of an equilateral triangle. The Hg-S bond distances were refined to 2.454(11) and 2.475(7) Å in the $\text{Hg}(\text{S}^n\text{C}_4\text{H}_9)_3^-$ and $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$ complexes respectively. The 1-butanethiolatomercury(II) complex is monomeric in dilute pyridine solution, but it dimerizes in concentrated solution. The Hg-S bond distance is 2.48(2) Å and the Hg-Hg distance is 3.69(5) Å in the $\text{Hg}_2(\text{S}^n\text{C}_4\text{H}_9)_2^{2+}$ complex. One or two pyridine molecules are, most probably, loosely coordinated to the mercury atoms, completing a distorted tetrahedral arrangement.

INTRODUCTION

Mercury(II) is well-known for its ability to form stable complexes with thiolates. The first mercury(II) thiolate complex was discovered by Zeise as early as 1834[1]. The structure of the $\text{Hg}(\text{SC}_n\text{H}_{2n+1})_2$, $n = 2, 3, 5-7$, complexes were in principle solved by Wells[2]. That work contains, however, only basic information like the coordination numbers of mercury. Detailed structures including one of those compounds, have later been reported for $\text{Hg}(\text{SCH}_3)_2$ [3], $\text{Hg}(\text{SC}_2\text{H}_5)_2$ [4], $\text{Hg}(\text{S}^n\text{C}_4\text{H}_9)_2$ [5] and $\text{Hg}(\text{S}^t\text{C}_4\text{H}_9)_2$ [6].

The structures of the compound series $\text{Hg}(\text{SR})(\text{CH}_3\text{CO}_2)$ have been reported for $\text{R} = \text{CH}_3$ [7], $\text{R} = {}^n\text{C}_3\text{H}_7$ and ${}^n\text{C}_4\text{H}_9$ [8], and $\text{R} = \text{C}_6\text{H}_5$ [9]. The alkanethiolate compounds consist of sulfur bridged ($-\text{Hg}-\text{SR}-\text{Hg}-\text{SR}-$) zig-zag chains linked to sheets by acetate bridges. It is noticeable that no monomeric HgSR^+ complexes have so far been found in the solid state.

Raman spectroscopic studies on aqueous solutions and aqueous/pyridine mixtures of $\text{HgSCH}_3(\text{CH}_3\text{CO}_2)$ have indicated predominance of dimeric $\text{Hg}_2(\text{SCH}_3)_2^{2+}$ complexes. In dilute mixtures, the $\text{Hg}_2(\text{SCH}_3)_2^{2+}$ complex dissociates to monoclear complexes with increasing pyridine content[7].

The structures of $(\text{C}_2\text{H}_5)_4\text{NHg}(\text{SC}_6\text{H}_5)_3$ and $((\text{C}_2\text{H}_5)_4\text{N})_2\text{Hg}(\text{SC}_6\text{H}_4\text{Cl-p})_4$ contain mononuclear tris and tetrakis(thiophenolato)mercurate(II) complexes respectively[10,11]. The $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$ complex is in the solid state trigonal-planar, while the $\text{Hg}(\text{SC}_6\text{H}_4\text{Cl-p})_4^{2-}$ complex is pseudotetrahedral. The structure of $(\text{C}_2\text{H}_5)_4\text{NHg}(\text{SCH}_3)_3$ is reported to consist of dimers with two bridging and four terminal thiolate groups[12].

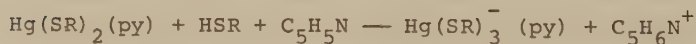
The purpose of this work was to examine the structures

of some mercury(II) thiolate complexes of varying stoichiometry, in solution. Pyridine was chosen as the solvent since mercury(II) thiolate compounds are sufficiently soluble only in strongly donating aprotic solvents. Moreover, the complex formation thermodynamics of some mercury(II) thiolate systems have recently been investigated in pyridine[13]. That study showed that three very strong mononuclear mercury(II) thiolate complexes are formed in pyridine solution; there are no indications of a fourth complex. The first and third complexes are predominating in large ranges of free ligand concentration, while the second complex, normally the most stable one never exceeds 45% of the total mercury(II) concentration.

Three mercury(II) thiolate complexes in pyridine were examined by means of large angle X-ray scattering (LAXS) technique on liquids. Two trithiolatomercurate(II) complexes, $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$ and $\text{Hg}(\text{S}^n\text{C}_4\text{H}_9)_3^-$, and the 1-butanethiolatomercury(II) complex, $\text{Hg}(\text{S}^n\text{C}_4\text{H}_9)^+$, have been studied in concentrated pyridine solutions at 25 °C.

EXPERIMENTAL

Preparation of solutions. The $\text{Hg}(\text{SR})_3^-$ complexes were prepared by adding an equivalent corresponding thiol to a mercury(II) thiolate solution according to



The HgSR^+ complex was prepared by dissolving equimolar amounts of $\text{Hg}(\text{SC}_4\text{H}_9)_2$ and $\text{Hg}(\text{C}_5\text{H}_5\text{N})_2(\text{ClO}_4)_2$ in warm pyridine, 60 °C; the mixture was slowly cooled down to room temperature. The composition of the studied solutions are given in Table I.

X-ray Scattering Measurements. The X-ray scattering from the free surface of the solutions was measured in a large angle theta-theta diffractometer[14] of Seifert GDS type. In order to avoid contact with the atmosphere and to avoid evaporation, the solutions were enclosed in a cylindrical thin-walled glass container, which was exactly half-filled. The absorption of the glass container and its angle dependence have previously been determined[15]. $\text{MoK}\alpha$ ($\lambda=0.7107 \text{ \AA}$) radiation was used as the X-ray source. The scattered intensities were determined at discrete points in the interval $4^\circ < \theta < 60^\circ$, separated by 0.0335 in $\underline{s}$, where $\underline{s} = 4\pi\lambda^{-1} \sin\theta$, and the scattering angle is 2θ . An extrapolation of the intensity data at $\theta < 4^\circ$ was necessary due to the upward meniscus in the glass container. A counting error of 0.35% was achieved by measuring $40\,000$ counts twice at each sampling point. The fraction incoherent scattering contributing to the intensities has been estimated in the usual manner[16].

Data Treatment. The same data reduction procedure and corrections as described previously were applied[16]. The experimental intensities were normalized to a stoichiometric unit of volume, containing one mercury atom. The scattering factors, corrections for anomalous dispersion and values for incoherent scattering were the same as used before[16]. The electric radial distribution functions (RDF), $\underline{D}(\underline{r}) - 4\pi\underline{r}^2 \rho_0$, were obtained by Fourier transformation from the intensity functions. The RDF's for the studied solutions are given in Fig. 1. Spurious peaks below $1.5 \text{ \AA}$ which could not be related to interatomic distances within the pyridine molecule or the perchlorate and thiolate ions have been removed by a Fourier transformation procedure[14].

All calculations were carried out by means of the computer programs

KURVLR[17] and STEPLR[18].

RESULTS

For the trithiolatomercurate(II) complexes a major peak in the RDF's is found at 2.5 Å. These peaks correspond to Hg-S bond distances, and the integral of the peaks indicates three Hg-S distances per mercury. Two minor peaks at about 3.8 and 4.3 Å correspond to Hg-C and S-S distances respectively, within the $\text{Hg}(\text{SR})_3^-$ complexes. The distances, the temperature factor coefficients of the Hg-S and Hg-C distances and the number of Hg-S distances were refined in the range $3.5 \leq \underline{s} \leq 13.5$ by a least-square refinement procedure. For the number of Hg-C distances and for the S-S distance, the pyridinum and thiolate ions and for free pyridine, fixed parameters were introduced. The parameters for the trithiolatomercurate(II) complexes are given in Table 2.

The radial distribution function for the $\text{HgSC}_4\text{H}_9(\text{ClO}_4)$ solution shows two distinct peaks at 2.5 and 3.7 Å, Fig 1. These peaks correspond to Hg-S and Hg-Hg distances respectively. The peak areas indicate two Hg-S and half a Hg-Hg distance per mercury. The peak at 3.7 Å, being somewhat unsymmetrical, also incorporates the expected Hg-C distance at around 3.8 Å. The distances and the temperature factor coefficients of the Hg-S and Hg-Hg distances have been refined in the range $4.0 \leq \underline{s} \leq 13.5$. The quality of the experimental intensities is not good enough to determine if any pyridine is loosely coordinated to mercury. The parameters for the bis(1-butanethiolato)dimercury(II) complex are given in Table 2. The parameters for the thiolate and perchlorate ions, and free pyridine have been taken from the literature and further refinements on these parameters have not been made.

DISCUSSION

The $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$ complex is found to be trigonal-planar in pyridine solution as well as in the solid state[10]. In the structure of $(\text{C}_2\text{H}_5)_4\text{NHg}(\text{SC}_6\text{H}_5)_3$ the HgS_3 entity is strongly distorted, but the average S-Hg-S angle is 120 degrees and the average Hg-S bond distance is 2.455 Å[10]. The Hg-S bond distance in the $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$ complex is 0.020 Å longer in pyridine solution than in the solid state. This increase in Hg-S bond distance is certainly due to the solvation of the $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$ complex in pyridine. Pyridine is a strong donor to the soft acceptor mercury(II)[19], though pyridine is a much weaker donor than thiolate ions. It has not been possible from current X-ray scattering data to determine whether or not pyridine molecules are coordinated to mercury in the $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$ complex. Pyridine has the possibility of solvating the mercury atom through the nitrogen atom and the phenyl rings through pi-interactions. The lengthening of 0.017 Å of the Hg-S bond in pyridine indicates that weak interactions between pyridine and mercury indeed occur, as only π -interactions should give a smaller effect. A similar lengthening of Hg-X bonds has been reported in the complexes HgX_3^- , X=Cl, Br, I, where solvent molecules are coordinated to mercury [20,21]. Two pyridine molecules are probably coordinated in the axial positions of a trigonal bipyramid.

The Hg-S bond distance is 0.02 Å shorter in $\text{Hg}(\text{S}^n\text{C}_4\text{H}_9)_3^-$ than in $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$, Table II. This is somewhat surprising since the $\text{Hg}(\text{SC}_6\text{H}_5)_3^-$ complex is the most stable of these complexes in pyridine solution[13]. The solvent interactions with a phenyl group is

approximately twice as strong as with a butyl group[22,23]. It is hard to tell if the Hg-S bond distance depends on either substantially weaker solvation of the butyl groups, or on smaller atom radius on the sulfur atom in the SC_4H_9^- ion than in SC_6H_5^- ion, or in fact, whether it depends on both factors.

The mononuclear $\text{HgSC}_4\text{H}_9^+$ complex exists in dilute pyridine solution[13]. This complex dimerizes when the concentration is increased. The structure of the $\text{Hg}_2(\text{S}^{\text{n}}\text{C}_4\text{H}_9)_2^{2+}$ complex is very similar to the units building the infinite chains in the structures of $\text{Hg}(\text{S}^{\text{t}}\text{C}_4\text{H}_9)_2$ [6] and $\text{Hg}(\text{S}^{\text{n}}\text{C}_4\text{H}_9)_2$ [5]. The Hg-S bond distance is 2.48(2) Å and the Hg-Hg distance is 3.69(5) Å. This means that the Hg-S-Hg angle is 96(3) degrees, and the S-Hg-S angle is 84 degrees if the Hg_2S_2 entity is co-planar, or somewhat smaller if the Hg_2S_2 entity is slightly out of planarity. Pyridine is definitely coordinated to mercury atoms in the $\text{Hg}(\text{S}^{\text{n}}\text{C}_4\text{H}_9)_2^{2+}$ complex. This study did not allow, however, the determination of either the number of coordinated pyridines or the Hg-N(pyridine) distance.

A change in the complex distribution can occur when the concentration is increased. The neutral copper(I) and silver(I) halide complexes in tetrahydrothiophene are monomeric in dilute solution while dimers or tetramers are formed in concentrated solution[24]. Already at 0.1 M this reaction starts. A mixture of Hg_2I^{3+} and HgI_2 complexes is formed in concentrated DMSO solutions with the Hg/I ratio one[20]. This reaction also starts at around 0.1 M. It is plausible that the HgSR^+ complexes in pyridine behave in a similar way.

ACKNOWLEDGEMENTS

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Table I. Composition (mol dm^{-3}), linear absorption coefficients, $\mu(\text{MoK}\alpha)$ (cm^{-1}) for the investigated solutions.

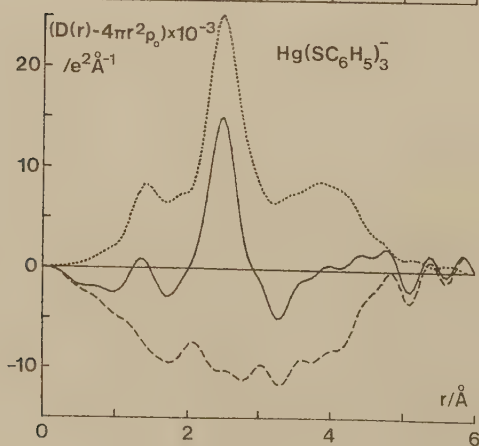
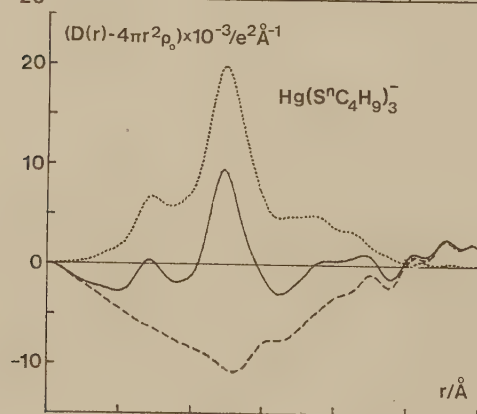
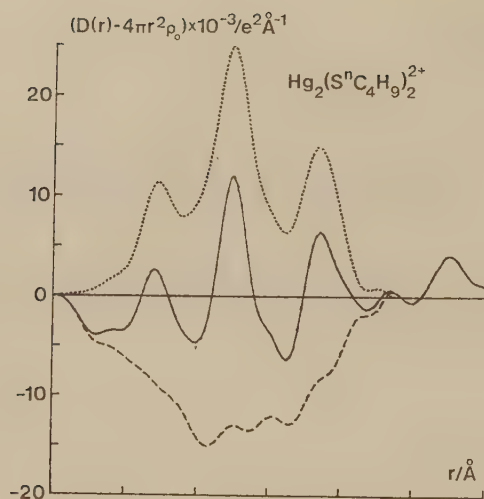
Solution	Hg	$\text{C}_5\text{H}_6\text{N}$	SR	ClO_4	$\text{C}_5\text{H}_5\text{N}$	μ
$\text{HgSC}_4\text{H}_9(\text{ClO}_4)$	0.600	—	0.600	0.600	9.2	15.5
$\text{C}_5\text{H}_6\text{NHg}(\text{SC}_4\text{H}_9)_3$	0.962	0.962	3.036	—	9.0	24.2
$\text{C}_5\text{H}_6\text{NHg}(\text{SC}_6\text{H}_5)_3$	0.889	0.889	2.9 9	—	9.0	22.3

Table II Interatomic distances, $\underline{d}(\text{\AA})$, temperature factor coefficients for the distances, $\underline{b}(\text{\AA}^2)$, and frequencies of the distances relative to one mercury atom, $\underline{n}$, for the $\text{Hg}_2(\text{SC}_4\text{H}_9)_2^{2+}$, $\text{Hg}(\text{SC}_4\text{H}_9)_3^-$ and $\text{Hg}(\text{SC}_6\text{H}_5)_3^+$ complexes in pyridine solution. The refined parameters are those with e.s.d.'s in parentheses.

Complex	Distance	$\underline{d}$	$\underline{b}$	$\underline{n}$
$\text{Hg}_2(\text{SC}_4\text{H}_9)_2^{2+}$	Hg-S	2.48 (2)	0.012 (3)	2.0
	Hg-Hg	3.69 (5)	0.023 (5)	0.5
	S-S	3.36	0.020	0.5
	Hg-C	3.75	0.022	2.0
$\text{Hg}(\text{SC}_4\text{H}_9)_3^-$	Hg-S	2.455 (11)	0.0179 (18)	3.1 (3)
	Hg-C	3.69 (7)	0.023 (9)	3.0
	S-S	4.25	0.020	3.0
$\text{Hg}(\text{SC}_6\text{H}_5)_3^+$	Hg-S	2.475 (7)	0.0072 (9)	3.0
	Hg-C	3.76 (4)	0.033 (7)	6.0
	S-S	4.29	0.020	3.0

LEGEND TO FIGURE

Fig.1. Experimental radial distribution function, $D(r)-4\pi r^2\rho_0$, for the 1-butanethiolatomercury(II) perchlorate, pyridinium Tris(1-butanethiolato)mercurate(II) and pyridinium tris(thiophenolato)mercurate(II) in pyridine solution (solid lines), model functions with parameters from Table II (dotted lines) and the differences between them (dashed lines).



VII

Mercury(II) Complexes with Tetrahydroselenophene
and Tetrahydrotellurophene. Vibrational Spectra

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Abstract: A number of complexes of the cyclic chalcogenoethers tetrahydroselenophene (THSe) and tetrahydrotellurophene (THTe) with mercury(II) halides and perchlorate were prepared. Their vibrational spectra were recorded and compared with the spectra of the corresponding tetrahydrothiophene (THT) complexes. Correlations between structural and spectroscopic data are discussed for the mercury(II) halide-THSe complexes.

INTRODUCTION

The Lewis basicity of inorganic mercury(II) compounds has been the topic for copious scientific work [1-12].

Complexes between mercury(II) compounds like halides, pseudo-halides, or salts, and uncharged organic nitrogen, phosphorus sulfur, selenium, or tellurium ligands are often very stable and have low solubility in water and many hard organic solvents, like alcohols, ketones, or ethers.

The complexes between mercury(II) and neutral organic sulfur donors have been eagerly studied for ligands like thiocarbamates [13-15], thioureas [16-21], and 6-mercaptopurine [22,23]. In these works, spectroscopic and crystallographic results have been reported. In all these ligands the donor atom is double bonded to a carbon atom. Since double bonds between selenium, or tellurium, and carbon atoms are comparably unstable, this type of ligands was little suitable for systematic comparisons of mercury(II) complexes with neutral group VI donor ligands.

The chalcogeno ethers $R\text{-Ch-R'}$ ($\text{Ch}=\text{S}, \text{Se}, \text{Te}$), however, are relatively stable even in the case of the selenium and tellurium compounds [10,24].

The preparation of many well defined mercury(II) complexes with thioethers and telluroethers, and of a few with selenoethers, has been reported [3,6,10,11]. The major part of them are addition compounds to mercuric halides of the general type $x\text{HgX}_2 \cdot y\text{RChR'}$ ($x, y=1-3$; $\text{Ch}=\text{S}, \text{Te}$; $\text{X}=\text{Cl}, \text{Br}, \text{I}$). Often only the composition and melting points were reported for these compounds, since they were used only as a means to characterize the chalcogeno ethers. In a number of investigations, however, the

structures, or vibrational spectra, of mercury(II) complexes with thioethers [25-40,42,43], selenoethers [40,41,43], and telluroethers [42-44] are reported. These investigations include results obtained with a number of cyclic or open chain ligands with one or several donor atoms.

The first study containing spectroscopic data on mercury(II) halide thioether, selenoether, and telluroether complexes, unless without complete assignments, was reported by Ferguson and Loh [43]. A systematic comparison of the behaviour of comparable sulfur, selenium, and tellurium ligands mercury(II) as metal acceptor, is still missing.

For that purpose, the pentacyclic chalcogenoethers tetrahydrothiophene (THT), tetrahydroselenophene (THSe), and tetrahydrotellurophene (THTe), were chosen in this work. They are sufficiently stable up to temperatures more than 100°C , their vibrational spectra are well known [45], and their structures in the gaseous state have been determined [46]. Several mercury(II) halide complexes with THT have been examined. The vibrational spectra of the $\text{Hg}(\text{THT})_2\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) in the solid state and in THT solution have recently been reported [47].

The structures of the THT complexes $\text{Hg}(\text{THT})_2\text{X}_2$ have been determined in THT solution for $\text{X}=\text{Br}, \text{I}$ [47] and in the solid state for $\text{X}=\text{Cl}, \text{Br}$ [48].

Mercury(II) chloride forms two well-defined and stable complexes with THT, $\text{Hg}(\text{THT})_2\text{Cl}_2$ and $\text{Hg}(\text{THT})\text{Cl}_2$. The crystal structure of the latter has been reported [4,29], and the FIR spectroscopic data are also known [30,49].

The crystal structures of the solid mercuric halide THSe complexes $\text{Hg}(\text{THSe})\text{Cl}_2$ and $\text{Hg}(\text{THSe})_2\text{X}_2$ ($\text{X}=\text{Br}, \text{I}$) will be reported elsewhere [50,51].

EXPERIMENTAL SECTION

Commercial tetrahydrothiophene (THT) was purified by distillation in a stream of dry nitrogen.

The tetrahydroselenophene (THSe) and tetrahydrotellurophene (THTe) were prepared according to literature methods [52-54].

Preparation of $\text{HgL}_x(\text{ClO}_4)_2$ ($\text{L}=\text{THT}; \text{THSe}, \text{THTe}; x=2-4$).

The solids were precipitated from a 50 mM stock solution of $\text{Hg}(\text{ClO}_4)_2$ in 90% aqueous methanol on addition of a tenfold excess of the liquid ligand. The obtained crystals were filtered off, washed with water, methanol and ether, and dried in vacuo. Well defined compounds were obtained by this method for THT and THTe, the one yielding a white solid $\text{Hg}(\text{SC}_4\text{H}_8)_2(\text{ClO}_4)_2$, the other small dirty yellow crystals of $\text{Hg}(\text{TeC}_4\text{H}_8)_4(\text{ClO}_4)_2$. The same procedure yielded white solid compounds of varying composition in the case of THSe, $\text{Hg}(\text{SeC}_4\text{H}_8)_x(\text{ClO}_4)_2$ ($2 < x < 3$). One of them, with an $x=2.5$, was chosen for further spectroscopic investigation (see below).

A well defined compound $\text{Hg}(\text{SeC}_4\text{H}_8)_3(\text{ClO}_4)_2$ was obtained on dropwise addition of the $\text{Hg}(\text{ClO}_4)_2$ stock solution to a mixture of excess THSe, diluted with no more than five times its own volume methanol.

The white crystals were filtered off, washed copiously with methanol and ether, and dried in vacuo.

Preparation of $\text{Hg}(\text{SeC}_4\text{H}_8)_x\text{X}_2$ Complexes.

The solid mercury(II) halide tetrahydroselenophene complexes were obtained on addition of a five-folded excess THSe to warm (70°C)

saturated solutions of the mercuric halides in acetonitrile. Large white crystals were obtained in all cases on slow cooling to room temperature.

From HgCl_2 the monocomplex $\text{Hg}(\text{SeC}_4\text{H}_8)\text{Cl}_2$ is formed; the remaining two mercuric halides prefer to add two THSe molecules to yield $\text{Hg}(\text{SeC}_4\text{H}_8)_2\text{Br}_2$ and $\text{Hg}(\text{SeC}_4\text{H}_8)_2\text{I}_2$, respectively. The solid complexes are relatively stable to redissociation, except the $\text{Hg}(\text{SeC}_4\text{H}_8)_2\text{I}_2$ that decomposes within less than 48 h when it is isolated and dried. It must therefore be stored under its saturated solution in acetonitrile.

Preparation of $\text{Hg}(\text{TeC}_4\text{H}_8)_x\text{X}_2$ Complexes

The preparation of the monotetrahydrotellurophene complexes was carried out following the method given by Morgan and Burstall [53]. The white to pale ivory coloured solids $\text{Hg}(\text{TeC}_4\text{H}_8)\text{Cl}_2$ and $\text{Hg}(\text{TeC}_4\text{H}_8)\text{Br}_2$ were eagerly washed with warm ethanol and dried in vacuo.

For elemental analyses (C,H, in some cases Hg) of the newly prepared solid compounds are given in Table I.

Spectroscopy

The IR spectra were recorded in the region $4000\text{--}250\text{ cm}^{-1}$ on a Perkin-Elmer 580B infrared spectrophotometer, connected to a Perkin-Elmer data station 3600, using nujol mulls between CsBr plates. One solution measurement was executed on the same instrument; the liquid was filled between two PE plates with an 0.5 mm spacer.

FIR spectra were recorded in the region $700\text{--}100\text{ cm}^{-1}$ on a Bruker 113V spectrometer on PE tablets.

Raman spectra were excited with the 647.1 nm line from a Kr^+ laser. The solids were sealed in narrow glass tubes, the solutions were prepared and stored in usual glass tubes.

The spectra were recorded on a Cary 82 and on a Spex Raman spectrophotometer equipped with a Kr-ion laser of Spectra Physics (Model 164), and on a D.I.L.O.R. RTI 30 Raman Spectrophotometer equipped with a triple monochromator, a d.c. amplifier and a Coherent Radiation Laboratories Innova 90-5 Kr-ion laser.

RESULTS

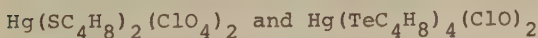
The bands observed in the spectra of the solids in the wave-number region below 750 cm^{-1} were collected in Table II with tentative assignments. The ligand modes were assigned according to a previous work [45], from which the bands observed on the liquid compounds at room temperature below 750 cm^{-1} were taken and included in Table II. The perchlorate modes were assigned following the treatment by Nakamoto [54].

Some structural data from literature [29,47-49,56], and from own investigations [50,51], were collected in Tables III and IV. The spectroscopic observations for which these results were of importance were included in the same Tables.

DISCUSSION

Perchlorate Compounds; $\text{HgL}_x(\text{ClO}_4)_2$ ($\text{L}=\text{THT}, \text{THSe}, \text{THTe}$; $x=2-4$).

The mercury(II) perchlorate forms stable solid complexes with all three cyclic chalcogeno ethers. The well defined compounds



were precipitated from an aqueous methanolic solution of the

perchlorate on addition of excess of the liquid ligand. On the other hand, the same procedure yielded precipitates $\text{Hg}(\text{SeC}_4\text{H}_8)_x(\text{ClO}_4)_2$ with compositions in the range $2 < x < 3$. When the $\text{Hg}(\text{ClO}_4)_2$ solution was slowly added to a large excess of THSe, however, the defined product $\text{Hg}(\text{SeC}_4\text{H}_8)_3(\text{ClO}_4)_2$ was obtained. It seems likely that the products with varying content of THSe are mixtures of at least two well defined products, probably $\text{Hg}(\text{SeC}_4\text{H}_8)_2(\text{ClO}_4)_2$ and $\text{Hg}(\text{SeC}_4\text{H}_8)_3(\text{ClO}_4)_2$. For spectroscopic investigations 4 compounds were chosen, three of them being the well defined complexes. The fourth of them was one of the $\text{Hg}(\text{SeC}_4\text{H}_8)_x(\text{ClO}_4)_2$, with x about 2.5. Some of the bands below 750 cm^{-1} (Table II) were assigned as pure ligand [45] or perchlorate [55] modes. The assignments of the remaining bands were based on the assumption that the coordination of the ligands around the mercury ions occurs linearly in $\text{Hg}(\text{THT})_2(\text{ClO}_4)_2$, trigonally planar in $\text{Hg}(\text{THTe})_3(\text{ClO}_4)_2$, and tetrahedrally in $\text{Hg}(\text{THTe})_4(\text{ClO}_4)_2$, the local symmetries around the mercury atoms being $D_{\infty h}$, D_{3d} , and T_d , respectively, the site symmetries being lower due to distortion and to the hydrocarbon rings on the chalcogene atoms.

In case of the nonstoichiometric compound " $\text{Hg}(\text{ClO}_4)_2 \cdot 2.5 \text{ THSe}$ " it is assumed that it consists of a mixture of equal parts of the well defined $[\text{Hg}(\text{THSe})_3](\text{ClO}_4)_2$ and a hypothetical $[\text{Hg}(\text{THSe})_2](\text{ClO}_4)_2$ which has not yet been isolated as a pure compound. It was therefore considered that one half of the mercury atoms in this mixed compound might be coordinated by three THSe in a trigonal planar arrangement of local D_{3d} , and that the other half of them are coordinated by two THSe at equal distances in a linear arrangement with local $D_{\infty h}$ symmetry, the site symmetry being lower in both cases.

For a linear three atom unit LHgL with point group $D_{\infty h}$ the following fundamental modes are expected:

$$\Gamma(\text{LHgL}) = 1 \Sigma_g^+(\text{Ra}) + 1 \Sigma_u^+(\text{IR}) + 1 \Pi_u(\text{IR}).$$

The symmetry reduction from the hydrocarbon chains introduces one or several additional vibrational modes into the system which are not expected for a pure three atom array, nor are pure internal ligand vibrations. They can be assigned to $\delta(\text{Hg-S-C})$ bending modes of unknown type of symmetry [33].

Moreover, the two directions perpendicular to the LHgL bond axis may become unequal, and the degeneracy of the Π_u modes is probably raised, the mode being split up into two different vibrations. The bands observed on the $[\text{Hg}(\text{THT})_2]^{2+}$ ion are assigned on these conditions. The IR bands at 307 cm^{-1} (Ra : 304 cm^{-1}) and 334 cm^{-1} are assigned to the $\nu_s(\Sigma_g^+)$ and to the $\nu_{as}(\Sigma_u^+)[\text{S-Hg-S}]$ stretching modes, respectively.

The relative intensities of the bands indicate that the THT-Hg-THT array belongs to one of the point groups C_{2h} or C_{2v} ; the selection rules for spectra of centrosymmetric molecules are almost strictly fulfilled. The correct races of the stretching modes of the $[\text{Hg}(\text{THT})_2]^{2+}$ would be $\nu_g(a_g)$ and $\nu_{as}(b_u)$ for point group C_{2h} or $\nu_s(a_1)$ and $\nu_{as}(b_2)$ for point group C_{2v} .

The bending modes are more difficult to assign; probably the IR band at 175 cm^{-1} and the Raman band at 186 cm^{-1} belong to (Hg-S-C) bending modes [33], while the Raman band at 161 cm^{-1} and the IR band at 207 cm^{-1} may belong to (S-Hg-S) bending modes of some kind. For the spectra of the compounds $[\text{Hg}(\text{TeC}_4\text{H}_8)_4](\text{ClO}_4)_2$ a local T_d symmetry was assumed around the mercury atoms.

For a five atomic tetrahedral entity HgL_4 with point masses L,

4 fundamentals would be expected:

$$\Gamma(\text{HgL}_4) = a_1(\text{Ra}) + e(\text{IR}) + 2f_2(\text{IR}, \text{Ra}).$$

For $[\text{Hg}(\text{TeC}_4\text{H}_8)_4](\text{ClO}_4)_2$ the HgL_4 stretching modes $\nu_2(a_1)$ ("pulsation") and $\nu_{as}(f_2)$ were assigned to the very strong, broad Raman band at 101 cm^{-1} (IR: 102 cm^{-1}) and the IR band at 112 cm^{-1} , respectively. The bending modes of type (e) and (f_2) were expected below 100 cm^{-1} , and were therefore not assigned.

In the $[\text{Hg}(\text{THSe})_3](\text{ClO}_4)_2$ complex the Raman band at 134 cm^{-1} is assigned to the $\nu_s(a_1)$ ("pulsation") stretching vibration. The Raman band at 181 cm^{-1} perhaps belongs to a $\delta(\text{Hg-Se-C})$ bending mode.

The Raman spectrum of the nonstoichiometric compound $\text{Hg}(\text{ClO}_4)_2 \cdot 2.5 \text{ THSe}$ contains an intense band at 137 cm^{-1} that indicates the presence of $[\text{Hg}(\text{THSe})_3]$ units in the material. Moreover, the spectrum contains one, even more intense, broad band at $156-7 \text{ cm}^{-1}$ and a weak, broad band at about $211-12 \text{ cm}^{-1}$. The latter two are assigned to a linear, or close to linear, $[\text{THSe-Hg-THSe}]^{2+}$ ion which should be relatively undistorted in the compound. Based on the same assumptions as for the $[\text{Hg}(\text{THT})_2](\text{ClO}_4)_2$, those two bands are assigned to a $\nu_s(\Sigma_g^+, a_1 \text{ or } a_g)$ and to a $\nu_{as}(\Sigma_u^+, b_2 \text{ or } a_u)$ stretching mode, respectively. Even in this case, the less intense band at $211-2 \text{ cm}^{-1}$ might alternatively belong to a $\delta(\text{Hg-Se-C})$ bending mode as well.

Mercuric Complexes of Type $\text{Hg}(\text{ChC}_4\text{H}_8)_2 \cdot \text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$; $\text{Ch}=\text{S}, \text{Se}$)
with Halogene-Bridged Double-Chain Structure

All three five membered ring type chalcogene ethers, THT, THSe, and THTe, readily precipitate the 1:1 complexes from solutions of mercury(II) chloride in ethanol or acetonitrile. The complexes

with THT and THTe have been described in the literature [4,29, 49,53].

The mercury(II) chloride complexes with THT and THSe are isomorphous [29,50], and isostructural with $(\text{Me}_3\text{P})\text{HgCl}_2$ [49,56].

The common structural principle is shown in Fig. 1; the hydrocarbon groups on the donor atoms were omitted. Selected distances for the three isostructural mercury(II) chloride complexes are given in Table III; atom numberings are consistent in Table III and Fig. 1.

As is seen in the figure, the solids are built up by double strings of almost linear $\text{Cl}_2^{\text{ii}}\text{-Hg-Cl}^{\text{i}}$ arrays. Each mercury(II) ion is coordinated by two chloride ions and one ligand molecule in an irregular triangle in the equatorial plane; the chloride ions in the axial positions belong to neighbour groups. Chloride ions of both terminal type (Cl_2) and of bridging type ($\text{Cl}_1, \text{Cl}_1^{\text{i}}, \text{Cl}_1^{\text{ii}}$) occur.

All these chlorides coordinate to the same mercury atom Hg1 on different distances (see Table III). For more details see [50].

Based on this structural information a treatment on the vibrational spectra of $\text{Hg}(\text{THT})\text{Cl}_2$, $\text{Hg}(\text{THT})\text{Br}_2$, and $\text{Hg}(\text{PMe}_3)\text{Cl}_2$ has been given in [49]. The following normal modes for the non-ligand vibrations were predicted based on a so called line group analysis:

$$\Gamma = 7a_g(\text{Ra}) + 7a_u(\text{IR})$$

and for the $\nu(\text{Hg-X}_2)$ and $\nu(\text{Hg-L})$ only:

$$\Gamma \nu(\text{Hg-X}_2) = a_g(\text{Ra}) + a_u(\text{IR}) \text{ and}$$

$$\Gamma \nu(\text{Hg-L}) = a_g(\text{Ra}) + a_u(\text{IR})$$

Unfortunately no Raman data were given for the $\text{HgX}_2\text{-THT}$ complex.

On this reason, a Raman spectrum of the $\text{Hg}(\text{THT})\text{Cl}_2$ was recorded, and assignments for this spectrum, and for the data from $\text{Hg}(\text{THSe})\text{Cl}_2$ were based on [49].

The spectroscopic data for $\text{Hg}(\text{THT})\text{Cl}_2$ and for $\text{Hg}(\text{PMe}_3)\text{Cl}_2$ [49] were included in the Table II and III in proper positions.

Nor or little coupling is expected between the stretching vibrations of the different Hg-Cl contacts.

For assignments of the Raman data on $\text{Hg}(\text{THT})\text{Cl}_2$ see Table III.

The intense Raman band at 305 cm^{-1} (IR: $306\text{--}7\text{ cm}^{-1}$) and the strong broad IR band at 186 cm^{-1} (Ra: 185 cm^{-1}) are assigned to the stretching vibrations of the Hg1-Cl2 and Hg1-Cl2 bonds in $\text{Hg}(\text{THSe})\text{Cl}_2$.

The Hg-Se stretching vibration is expected to show little or no coupling at all, and the strong Raman band at 237 cm^{-1} was assigned to this fundamental according to [41].

The Raman band at 211 cm^{-1} may be assigned to a $\delta(\text{Hg-Se-C})$ or a $\delta(\text{Cl-Hg-Se})$ bending mode. All these assignments are, however, uncertain. A final decision is still outstanding.

The assignment of the remaining bands below 300 cm^{-1} is even more uncertain. The Raman bands at 159, 129-30 and 141 cm^{-1} lie in the typical region where stretching as well as bending modes for medium to long range Hg-Cl contacts have been reported [49].

Moreover, Konovalov and Davarski [57] pointed out that a correlation exists between the length of a Hg-Cl interaction and the wavenumber of its stretching vibration. On comparison with their results, the bands at 159, 129-30 and 141 cm^{-1} may be assigned to the stretching vibrations of the $\text{Hg1-Cl1}^{\text{i}}$ and the $\text{Hg1-Cl1}^{\text{ii}}$ bonds, or to some modes of type a_g which are obtained from them by coupling. Probably one of them belongs to some kind of bending or chain mode. Generally speaking, too little is still

known, and has been reported, about the vibrational spectra of this type of double chains to allow a complete treatment of the spectroscopic material. Thus all the assignments which are suggested above are tentative and to a high degree unsure.

Mercuric Halide Complexes of Type $\text{Hg}(\text{TeC}_{4-8}\text{H}_2)_X$ ($X=\text{Cl}, \text{Br}$) with Unknown Structure

THTe yields the 1:1 complexes with mercury(II) chloride [53] and bromide under the reported preparation conditions.

The structures of these THTe complexes are still unknown, but their low solubility in common organic solvents indicates some type of a polymer structure similar to those found for HgLC_2 ($L=\text{THT}, \text{THSe}, \text{PR}_3$) [4, 29, 49, 50, 56]. They are probably not isostructural with the compounds in the previous section [58].

Their spectral data are in good agreement with those from compounds consisting of halogene bridged dimers of edge-linked tetrahedra with ligands in trans-positions (see [3, 49, 59]).

On the other hand, the spectra are even closely related to those of compounds built up of chains formed by halogene bridges, with all mercury atoms coordinated by one ligand molecule L , and four bridging halogenes. This type of polymer is found in e.g.

$\text{Hg}(\text{PEt}_3)\text{Cl}_2$ [56], and is related to, but different from, that in $\text{Hg}(\text{THT})\text{Cl}_2$ and $\text{Hg}(\text{THSe})\text{Cl}_2$.

The differences between the two types of structures have been excellently described in the literature [3, 59]. In [3] and [56] it is shown how both polymeric structures can be derived from an infinite array of dimeric units of the above mentioned type.

The close relationship between the "isolated" dimers and the polymer chains which can be built up with them makes it

impossible to decide whether a compound possesses the one or the other structure, based only on vibrational spectra. The spectroscopic data were evaluated outgoing from the assumption that the compounds have one of these structures. The mercury(II) tellurium bond was expected to give rise to a very intense bands in the Raman and IR spectra. On this assumption the strong Raman bands at $146\text{-}7\text{ cm}^{-1}$ from the chloride and at 134 cm^{-1} for the bromide were assigned to that vibration according to [44].

One alternative which also is supported by literature [43] might be to assign the Hg-Te stretching modes to weaker bands at 122 cm^{-1} (Raman) for the chloride and at about 125 cm^{-1} (IR) for the bromide. A strong IR band at 288 cm^{-1} and a broad, less intense Raman band at 277 cm^{-1} are assigned to Hg-Cl stretching modes of type (a_u or b_g) and $\nu_s(a_g)$, respectively. Similarly, the bands at 189 cm^{-1} (IR) and 185 cm^{-1} (Raman) are assigned to Hg-Br stretching modes $\nu_{as}(a_u \text{ or } b_g)$ and $\nu_s(a_g)$. The bands at about 200 cm^{-1} (Ra) and 210 cm^{-1} (IR), and the Raman band at 122 cm^{-1} , may belong to stretching or bending modes in the Hg-Cl-Hg' bridges [49].

Analogously it is suggested that the strong broad IR band at about 149 cm^{-1} and the weak IR band at ca 125 cm^{-1} in the bromide belong to some stretching or bending mode in the Hg-Br-Hg' bridges. All these assignments would be in good agreement with a polymeric halogene bridged structure of the type which has been reported for the 1:1 complexes of mercury(II) chloride with triethylphosphine (PET_3) and 2,4,6-trimethylpyridine [49,56], but also a dimeric structure.

Any decision whether the title compounds have the one, the other, or some different structure, could not be derived from the spectroscopic material (see above).

Halide Complexes $\text{Hg}(\text{SeC}_4\text{H}_8)_2\text{X}_2$

Under the reported conditions of preparation the mercury(II) bromide and iodide add two THSe molecules per formula unit. They are built up of isolated pseudotetrahedral L_2HgX_2 molecules [51].

Thus they are comparable to the corresponding compounds $\text{HgX}_2 \cdot 2\text{THT}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), for which the structure in THT solution (Br, I) and in the solid state (Cl, Br) and the vibrational spectra on the solutions and the solid compounds have been determined, and will be reported by Sandström, Persson, and (in parts) Goggin [48, 49]. Some of the results are useful for the assignment and treatment of the spectroscopic data obtained from the solid THSe complexes, and have therefore been collected in Table IV.

Some interatomic distances determined crystallographically for the $\text{HgX}_2(\text{THSe})_2$ ($\text{X} = \text{Br}, \text{I}$) groups are included in the same Table. The deviation of the molecular structure from ideal tetrahedral coordination is small, and assignments of the observed bands can therefore be based in good approximation on an assumed C_{2v} point group symmetry.

The coordination of Hg1 in $\text{Hg}(\text{SeC}_4\text{H}_8)_2\text{I}_2$ is shown in Fig. 2 as an example (compare [51]).

The following normal modes are expected for a five-atomic pseudotetrahedral array L_2HgX_2 of point masses:

$$\Gamma(\text{L}_2\text{HgX}_2) = 4a_1(\text{IR}, \text{Ra}) + a_2(\text{Ra}) + 2b_1(\text{IR}, \text{Ra}) + 2b_2(\text{IR}, \text{Ra})$$

or, if the internal bending modes are withdrawn, for stretching modes only:

$$\Gamma_v = 2a_1(\text{IR,Ra}) + b_1(\text{IR,Ra}) + b_2(\text{IR,Ra})$$

In the bromide compound, the IR bands at around 215 cm^{-1} and at 196 cm^{-1} (Raman: 196 cm^{-1}) are assigned to the antisymmetric $\nu_{\text{as}}(b_1)$ and the symmetric $\nu_{\text{s}}(a_1)$ Hg-Se stretching modes, respectively.

The $\nu_{\text{s}}(\text{Br-Hg-Br})$ of type a_1 , however, was observed as a sharp, very strong Raman band at 158 cm^{-1} . The bands in the lower wave-number region belong most probably to Br-Hg-Br and Se-Hg-Se banding modes.

In the corresponding iodine compound $\text{HgI}_2 \cdot 2\text{THSe}$, the assignments are uncertain since only two nonligand bands were observed in the Raman spectrum above 100 cm^{-1} .

These two bands, the very strong band at 127 cm^{-1} and a broad shoulder at about 145 cm^{-1} , were tentatively assigned to the symmetric $\nu_{\text{s}}(a_1)$ and the antisymmetric $\nu_{\text{as}}(b_2)$ I-Hg-I stretching vibrations.

There are no indications for Hg-Se stretching modes in this spectrum. Due to the extremely high sensitivity of the compound towards redissociation, no FIR spectrum was recorded. It is therefore assumed that the Hg-Se stretching vibrations may be observable in that spectrum. The presence of the ligand in the compound is proved by the crystal structure [51], and by the presence of the pure ligand modes in the Raman and IR spectra (see Table II). The positions of the mercury-halide stretching modes correlate well with the Hg-X distances, as can be shown by comparison with some other compounds with the same type of structure (Table IV).

All these results fit well with the concept of Konovalov and Davarski [57] which was mentioned above.

Solutions of mercury(II) halides HgX_2 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) in THSe

It was expected that the complexation behaviour of the mercury(II) halides in liquid THSe should be similar to that in liquid THT. The formation of pseudotetrahedral mononuclear complexes $\text{Hg}(\text{THT})_2\text{X}_2$ in THT solutions had been found by Persson and Sandström [47] for $\text{X} = \text{Cl}, \text{Br}, \text{I}$.

Saturated solutions of the mercury(II) halides in THSe were prepared, and Raman spectra were recorded in the low wavenumber region. In the case of HgCl_2 dissolved in THSe, an IR spectrum was recorded as well.

The non-solvent bands obtained from the spectra of these solutions were included in Table II at suitable places.

The broad weak Raman bands at 255 cm^{-1} (IR: 249 cm^{-1}) for HgCl_2 , at 177 cm^{-1} for HgBr_2 , and at 135 cm^{-1} for HgI_2 in THSe solutions were assigned to the symmetric $\nu_s(a_1)\text{Hg-X}$ stretching vibrations. No solvent-mercury vibration modes were observed.

CONCLUSIONS

As has been seen throughout the paper, the mercury(II) halides often behave very similarly towards THSe and THT. Spontaneously the same solid complexes are formed, with identical, or very similar, structural and spectroscopic properties. The only difference was stated for the mercuric chloride complexes. With THT, two well defined complexes $\text{HgCl}_2 \cdot x\text{THT}$ ($x = 1$ or 2) have been prepared; their crystal structures have been solved [4, 29, 48]. The 1:2 complex is, however, less stable than 1:1 complex. Any formation of a 1:2 complex between HgCl_2 and THSe has not yet been stated. On the other hand, the differences between complexes or mercury(II) halides with THSe or THTe seem

to be more serious. Both HgCl_2 and HgBr_2 prefer to form 1:1 complexes with THTe; from their spectral data, and from X-ray powder diffraction, it is assumed that the compounds are not isostructural to $\text{HgCl}_2 \cdot \text{THT}$ and $\text{HgCl}_2 \cdot \text{THSe}$. One similarity might be that even the THTe complexes probably possess a halogen bridged polymer structure, which is related to that of the THT and THSe 1:1 complexes (see text).

In the field of the perchlorates the picture is slightly different. Meanwhile $\text{Hg}(\text{ClO}_4)_2$ likes to add two THT molecules per metal ion, it prefers to coordinate four THTe molecules per mercury(II). In the case of THSe as ligand system, the two cations $[\text{Hg}(\text{THSe})_2]^{2+}$ and $[\text{Hg}(\text{THSe})_3]^{2+}$ seem to have comparable stability, and thus mixed compounds are formed. When the mercury(II) acceptor ions are not coordinated by halogene ions, the selenium ligand seems to take a position in the middle between the two extremes sulfur and tellurium. This is what might be expected from their positions in the periodic system.

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Table I: Analytical Data

Compound	calculated			found		
	%C	%H	%Hg	%C	%H	%Hg
Hg(THT) ₂ (ClO ₄) ₂	16.69	2.80	34.84	17.2	2.78	
Hg(THSe) ₃ (ClO ₄) ₂	17.91	3.01	24.93	17.9	2.97	
Hg(THSe) _{2.5} (ClO ₄) ₂ ^a	16.29	2.73	27.21	16.4	2.60	
Hg(THTe) ₄ (ClO ₄) ₂	16.94	2.84	17.68	16.9	2.80	
Hg(THSe)Cl ₂	11.82	1.98	49.34	11.8	1.98	48.3
Hg(THSe) ₂ Br ₂	15.24	2.56	31.81	15.1	2.49	31.2
Hg(THTe)Cl ₂ ^b	10.55	1.77	44.07	10.8	1.77	46.2
Hg(THTe)Br ₂	8.83	1.48	36.86	8.8	1.49	

^a see text for explanation.

^b first synthesis reported in [53].

Fig.1: Halogene-Bridged Chain Structure in $\text{Hg}(\text{THT})\text{Cl}_2$ [29], $\text{Hg}(\text{THSe})\text{Cl}_2$ [50], and $\text{Hg}(\text{PMe}_3)\text{Cl}_2$ [49,56].

The carbon and hydrogen atoms on the ligand donor atoms have been omitted. For numbering of the atoms compare Table III and [50]. Two repeat units are shown.

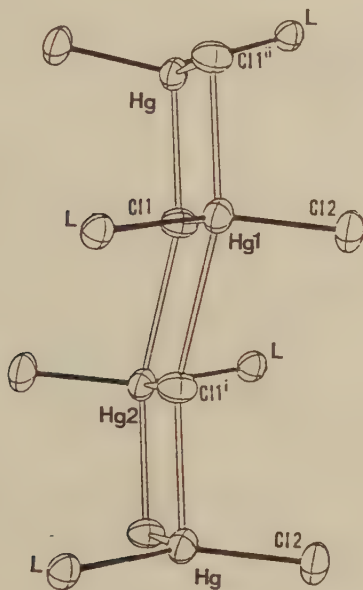


Fig.2: Molecular Structure of the Complexes $\text{Hg}(\text{THSe})_2\text{X}_2$ ($\text{X}=\text{Br}, \text{I}$). The environment of mercury atom Hg1 in $\text{Hg}(\text{THSe})_2\text{I}_2$ has been chosen as example (see text). For atom numbering see Table IV and [51].

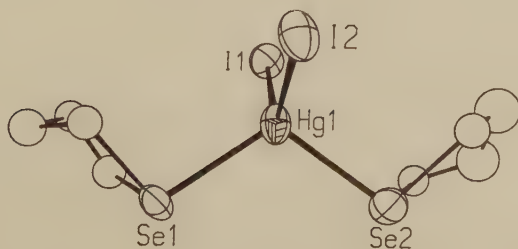


Table II:^a Vibrational Spectroscopic Data for Some Mercury(II) THT, THSe, and THTe Complexes. The bands observed in the region 750-100cm⁻¹ are given. All assignments, except those from literature, are tentative. Alternatives to assignments are given in italics.

Sample	internal ligand modes ^b						perchlorate modes ^c	
		ν_{27}	ν_{11}	ν_1	ν_{18}	ν_{19}	ν_2	ν_4
THT ^d	IR			472 vw	518 m		686 m	
	Ra	294 vw		471 ms	519 wm		687 vvs	
THSe ^d	IR			363 w	480 w	587 w	614 w	
	Ra	260 vvw		363 s	481 m	588 s	616 vvs	
THTe ^d	IR				445 wm	545 m	565 vw	
	Ra	160 vvw,b	297 sh	310 s	442 s	543 s	561 vvs	
Hg(THT) ₂ (ClO ₄) ₂	IR		419 vw	477 w	516 m	643 sh	650 m,b	461 w
			428 m					619 s
	FIR		425 w	477 m	516 s	644 w	651 m	625 sh
	Ra	280 sh,b		475 w	516 w		650 s	622 vs,b
Hg(THSe) ₃ (ClO ₄) ₂	IR			359 m	477 m	577 m	601 m	455 vw
	Ra			362 s	478 m	579 m	601 vs	458 w
Hg(THSe) _x (ClO ₄) ₂	IR			359 w	472 m,b	572 m	591 m	624 vs
	Ra			359 m	472 m,b	573 w	590 s,b	623 vs,b
Hg(THTe) ₄ (ClO ₄) ₂	IR				445 m	544 m	562 w	620 vs,b
	FIR	167 m,b	291 w,b	312 w,b	443 s,b	541 s	560 m	455 w
Hg(THT)Cl ₂			298 sh	316 s	447 s	546 m	564 s	456 sh
	FIR ^f							623 w
Hg(THSe)Cl ₂	Ra			476 w	518 w,b		660 s	
	IR			357 w	475 s	572 m	595 s	
	FIR			357 s	475 s	571 s	595 vs	
	Ra			363 vs	475 vs	581 s	603 vs	
Hg(PMe ₃)Cl ₂ ^g	FIR							
	Ra							
Hg(THTe)Cl ₂	IR				446 m	547 s	568 w	
	FIR	172 m,b		312 sh	445 m	546 s	566 m	
	Ra			314 s	448 s	547 m	568 s	
Hg(THTe)Br ₂	IR				444 w	542 m	565 vw	
	FIR		287 vw		443 s	542 vs	550 sh	
	Ra			312 s	443 ms	543 wm	561 w	
Hg(THSe) ₂ Br ₂	IR						567 s	
	FIR			357 w	472 s	572 s,b	601 m	
	Ra			358 m	474 s	577 s	592 s	
Hg(THSe) ₂ I ₂	IR			362 s	476 s	579 ms	603 vs	
	Ra			356 vw	474 w	579 m	602 w	
HgCl ₂ in THSe ^h	IR			361 ms	477 wm	582 wm	602 ms	
	Ra							
HgBr ₂ in THSe	Ra							
HgI ₂ in THSe	Ra							

^a In this Table the following abbreviations for relative intensities have been used: w=weak, m=medium, s=strong, v=very, sh=shoulder, b=broad, wm= weak to medium, ms= medium to strong.

^b For numbering and assignments of the ligand modes see [45].

^c For numbering and assignments of the perchlorate modes see [55].

^d Data from [45].

^e x $\approx$ 2.5 (compare text).

^f FIR data and assignments taken from [49].

^g From [49].

^h Solution data; the internal modes of the solvent THSe have been omitted.

Hg-L stretching modes

 ν_s ν_{as}
Hg-X stretching modes (X=Cl,Br,I)
(for explanation see text)bending modes and unassigned
bands (see text)

307 m 333 w

307 w 334 m

304 vs
310 sh,b

134 vvs 181 vw

137 s
156-7 s,b 211-2 vw,b102 vs 112 s
101 vvs

279 m

277 vs 322 s 197 s 164 s 134 s
312 sh 124 sh

311 s

195 sh

170 s,b

306 vs,b

307 vs,b

305 vs

188 s,b

189 vw

159 vs

141 s

129 s

363 w 361 w

300 s

141 s,b

124 s

115 s

291 s

142 sh

136 m

112 m

288 vs,b

277 m,b

210 m,b

200 m,b

(146-7 vs)

122 s

(125 w,b) (125 w, b)
(149 vs,b)

189 m,b

149 vs,b

125 w,b

135 vvs

185 m,b

(135 vvs)

196 vs,b 215 sh,b
196 m,b

158 vvs (139-40 ms)

145 sh,b 127 vvs

249 vw,b

255 vw,b

177 vw,b

135 wm

207 m, 203 sh, 175 w,b

186 vs, 161 m

(181 vw)

(211-2 vw,b)

(167 m,b)

325 sh,b, 298 sh,b
211 w, (141 s, 129 s)(124 s, 115 s)
(136 m, 112 m)(210 m,b, 172 m,b)
(200 m,b, 122 s)

(125 w,b)

127 m,b
139-40 ms, 124 m

Table III: Selected Structural and Spectroscopic Data on a Series of Isostructural 1:1 Complexes of Mercury(II) Chloride. Values from Raman measurements are in italics. The atom numbering is the same as in Fig. 1 and in [50].

Complex:	Hg(SC ₄ H ₈)Cl ₂	Hg(SeC ₄ H ₈)Cl ₂	Hg(PMe ₃)Cl ₂
distances(pm)			
Hg-L	240 ^{<u>d</u>}	253.5 ^{<u>b</u>}	236.5 ^{<u>c</u>}
Hg-Cl ₂	230 ^{<u>d</u>}	235.5 ^{<u>b</u>}	235.5 ^{<u>c</u>}
Hg-Cl ₁	262 ^{<u>d</u>}	263.4 ^{<u>b</u>}	278.2 ^{<u>c</u>}
Hg-Cl ₁ ^{<u>i</u>}	307 ^{<u>d</u>}	316.5 ^{<u>b</u>}	348.9 ^{<u>c</u>}
Hg-Cl ₁ ^{<u>ii</u>}	283 ^{<u>d</u>}	284.2 ^{<u>b</u>}	294.1 ^{<u>c</u>}
stretching vibrations (cm ⁻¹)			
Hg-L	279(277) ^{<u>d</u>}	(237) ^{<u>e</u>}	361(363) ^{<u>f</u>}
Hg-Cl ₂	322,312(311) ^{<u>d</u>}	307(305) ^{<u>e</u>}	300(291) ^{<u>f</u>}
Hg-Cl ₁	197(195) ^{<u>d</u>}	188(189) ^{<u>e</u>}	
Hg-Cl ₁ ^{<u>i</u>} g	134,124 ^{<u>d</u>}	(141), (129) ^{<u>e</u>}	
Hg-Cl ₁ ^{<u>ii</u>}	164(170) ^{<u>d</u>}	(159) ^{<u>e</u>}	141(142) ^{<u>f</u>}

^a from [29], ^b from [50], ^c from [49] and [56]

^d IRdata from [49] Raman data: this work, ^e this work

^f from [49] ^g for tentative assignments in the low wavenumber see in the text.

Table IV: Selected Structural and Spectroscopic Data on a Series of Pseudotetrahedral L_2HgX_2 Complexes. Values from Raman measurements are given in italics. The atom numbering is the same as in Fig.2.

Complex	$Hg(SC_4H_8)_2Br_2$ (solid)	$HgBr_2$ in THT solution	HgI_2 in THT solution	$Hg(SeC_4H_8)_2Br_2$ (solid)	$Hg(SeC_4H_8)_2I_2$ (solid)
distances (pm)					
Hg-L ₁	259.1 ^a	262 ^b	272 ^b	267.2 ^c	Hg1 Hg2 268.0 ^c 274.8 ^c
Hg-L ₂	260.4 ^a	262 ^b	272 ^b	262.0 ^c	268.8 ^c 270.1 ^c
Hg-X ₁	254.1 ^a	253.5 ^b	267 ^b	260.9 ^c	278.6 ^c 271.8 ^c
Hg-X ₂	256.4 ^a	253.5 ^b	267 ^b	259.6 ^c	274.1 ^c 272.8 ^c
stretching vibrations (in cm ⁻¹)					
ν_{as} [Hg-L] (b_1)	296 ^b			215 ^d	
ν_s [Hg-L] (a_1)				196(196) ^d	
ν_{as} [Hg-X] (b_2)	183(184) ^b	211 ^b	177 ^b		
ν_s [Hg-X] (a_1)	170(159) ^b	(179) ^b	(140.5) ^b	(158) ^d	(127) ^d

^a from [48], ^b from [47], ^c from [51], ^d this work.

